Journal of the Chemical Society

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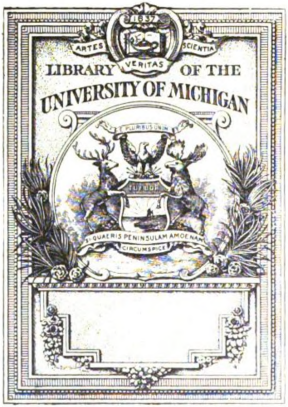
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THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS
ON
ORGANIC CHEMISTRY.

1197.

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REPORT OF

THE INTERNATIONAL COMMITTEE

ON ATOMIC WEIGHTS.

In the year 1900 an International Committee on atomic weights was organized, composed of more than fifty representatives from chemical and other societies. Its conferences were necessarily conducted by correspondence, and the delays and difficulties of the work proved to be both serious and annoying. Accordingly, the Committee, by vote, designated a smaller body of three representatives, and the latter now has the honour to report its recommendations.

On the fundamental question of standards, definite and formal action seems to be impracticable. By the original committee of the German Chemical Society, the oxygen standard was adopted, but that proposal, whilst receiving strong support, also met with serious opposition. In fact, opinion, as expressed by individual voices, seems to be somewhat evenly divided upon this question, and around it there has already grown up a controversial literature of formidable proportions. To force the adoption of either standard, oxygen, or hydrogen, appears therefore to be impossible, and for some time to come both are likely to be employed. Between them, experience must be the final arbiter. That standard which best serves to co-ordinate chemical and physical knowledge will ultimately be chosen, and the other will gradually fall into disuse. Meanwhile, it is important that the most probable values for the several atomic weights should be indicated, and that every table of them should be consistent within itself. Such a table has been prepared by our distinguished predecessors and its revision, as knowledge advances, seems to be our proper function.

In order that our work may be of the most general service, we have prepared a table in which both standards of atomic weight are represented. In most of its details it is identical with the table which was reported by the previous committee at the beginning of the year 1902.* Some changes, however, have, in our judgment, become necessary, and these may be briefly indicated as follows:

Antimony.—In the former reports of the committee, the value derived by Cooke from analyses of the bromide, Sb = 120, was adopted.

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* In No. 1 of the *Berichte* for 1902.

This, however, ignores the work of Cooke and of Schneider upon antimony trisulphide, and the still more recent determinations made by Friend and Smith. The true number being therefore in doubt, we recommend the use of an average value, and put Sb = 120·2.*

Germanium.—The number 72·5 is more nearly in accord with Winkler's determinations than the former number 72.

Hydrogen.—In the column which represents the oxygen standard, hydrogen has heretofore been assigned the value 1·01. The number 1·008 is, however, much more exact, and the error in 1·01 is too large to be perpetuated. Each figure should be given to the nearest *significant* decimal.

Lanthanum.—During 1902, two new determinations of the atomic weight of lanthanum were published. According to Jones, La = 138·77. Brauner and Pavlíček found La = 139·04. Both investigations were conducted with great skill and care, and each one seems to have some points of advantage over the other. The average La = 138·9 appears to be the safest value to adopt. These data naturally influence our judgment in the case of cerium, and we retain Brauner's number, Ce = 140, rather than adopt the lower estimates made by other observers.

Mercury.—Taking into account all the determinations which have appeared, and giving great weight to the most recent measurements by Hardin, we regard the value Hg = 200 as best warranted by the existing evidence.

Palladium.—The atomic weight of this metal is in doubt. The best determinations give values ranging from 106 to 107. The mean between them, Pd = 106·5, has been provisionally adopted.

Radium.—This element appears in the table for the first time. Madame Curie's determination of the atomic weight, Ra = 225, is probably not far from the truth.

Selenium.—Judging from the work of Lenher, and the very recent determinations by Jul. Meyer, the former value, Se = 79·1, is probably too low. In order to give due weight to the newer measurements, we write Se = 79·2.

Tin.—The determinations by Bongartz and Classen, which seem to be the best, make Sn = 119. The former value, 118·5, is almost certainly too low.

Uranium.—According to the very recent investigation by Richards and Merigold, the atomic weight of uranium is 238·5.

Zirconium.—The figure Zr = 90·6 is apparently the most probable.

In thus assuming the duties assigned to us by the larger International Committee, we act upon the conviction that the purpose of our appointment is to secure the promptness and efficiency which is only possible with a comparatively small working body. In order to carry out this purpose, we must depend upon the co-operation and assistance of our colleagues. We therefore beg that they, and also all other chemists who are interested in researches upon atomic weights, will aid us with their criticisms and advice. We especially ask that publications upon the subject shall be sent to us, in triplicate if possible, so that no matter of importance may be overlooked. Without support of this kind our work cannot be made fully effective.

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* O = 16.

The complete table of atomic weights, with foregoing changes incorporated, follows.

F. W. Clarke }
T. E. Thorpe } *Committee.*
Karl Seubert }

1903.

INTERNATIONAL ATOMIC WEIGHTS.

		O=16.	H=1.
Aluminium	Al	27·1	26·9
Antimony	Sb	120·2	119·3
Argon	A	39·9	39·6
Arsenic	As	75·0	74·4
Barium	Ba	137·4	136·4
Bismuth	Bi	208·5	206·9
Boron	B	11	10·9
Bromine	Br	79·96	79·36
Cadmium	Cd	112·4	111·6
Cæsium	Cs	133	132
Calcium	Ca	40·1	39·8
Carbon	C	12·00	11·91
Cerium	Ce	140	139
Chlorine	Cl	35·45	35·18
Chromium	Cr	52·1	51·7
Cobalt	Co	59·0	58·56
Columbium (Niobium)	Cb	94	93·3
Copper	Cu	63·6	63·1
Erbium	E	166	164·8
Fluorine	F	19	18·9
Gadolinium	Gd	156	155
Gallium	Ga	70	69·5
Germanium	Ge	72·5	71·9
Glucinum (Beryllium)	Gl	9·1	9·03
Gold	Au	197·2	195·7
Helium	He	4	4
Hydrogen	H	1·008	1·000
Indium	In	114	113·1
Iodine	I	126·85	125·90
Iridium	Ir	193·0	191·5
Iron	Fe	55·9	55·5
Krypton	Kr	81·8	81·2
Lanthanum	La	138·9	137·9
Lead	Pb	206·9	205·35
Lithium	Li	7·03	6·98
Magnesium	Mg	24·36	24·18
Manganese	Mn	55·0	54·6
Mercury	Hg	200·0	198·5

		O = 16.	H = 1.
Molybdenum	Mo	96·0	95·3
Neodymium	Nd	143·6	142·5
Neon	Ne	20	19·9
Nickel	Ni	58·7	58·3
Nitrogen	N	14·04	13·93
Osmium	Os	191	189·6
Oxygen	O	16·00	15·88
Palladium	Pd	106·5	105·7
Phosphorus	P	31·0	30·77
Platinum	Pt	194·8	193·3
Potassium	K	39·15	38·86
Praseodymium	Pr	140·5	139·4
Radium	Ra	225	223·3
Rhodium	Rh	103·0	102·2
Rubidium	Rb	85·4	84·8
Ruthenium	Ru	101·7	100·9
Samarium	Sm	150	148·9
Scandium	Sc	44·1	43·8
Selenium	Se	79·2	78·6
Silicon	Si	28·4	28·2
Silver	Ag	107·93	107·12
Sodium	Na	23·05	22·88
Strontium	Sr	87·6	86·94
Sulphur	S	32·06	31·83
Tantalum	Ta	183	181·6
Tellurium	Te	127·6	126·6
Terbium	Tb	160	158·8
Thallium	Tl	204·1	202·6
Thorium	Th	232·5	230·8
Thulium	Tm	171	169·7
Tin	Sn	119·0	118·1
Titanium	Ti	48·1	47·7
Tungsten	W	184·0	182·6
Uranium	U	238·5	236·7
Vanadium	V	51·2	50·8
Xenon	X	128	127
Ytterbium	Yb	173·0	171·7
Yttrium	Yt	89·0	88·3
Zinc	Zn	65·4	64·9
Zirconium	Zr	90·6	89·9

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.
6. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
7. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
8. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

9. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

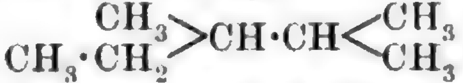
10. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

11. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ*.

12. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

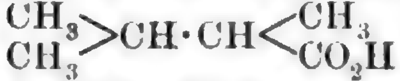
13. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ α-cyanopropane.

14. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,



$\begin{matrix}CH_3\\CH_3\cdot CH_2\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$ or $CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$

should be termed βγ-dimethylpentane, not methylethyl*iso*propylmethane, and



$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CO_2H\end{matrix}$ or $CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$

should be termed αβ-dimethylbutyric acid, not αββ-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

15. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

16. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisoil, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

17. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

18. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt{\cdot}CHMe{\cdot}CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3{\cdot}CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc{\cdot}CHMe{\cdot}CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6HEt_2(OH)_2{\cdot}CO_2H$, and not $C_6H_3(OEt)_2{\cdot}CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}CO_2H$.

19. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

20. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, β-anilino-acrylic acid, $NHPh{\cdot}CH{:}CH{\cdot}CO_2H$, α-iminopropionic acid, $NH{:}CMe{\cdot}CO_2H$.

21. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

22. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

23. The Collective Index, 2nd decade (1883—1892) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

24. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

25. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

26. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

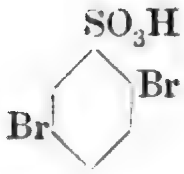
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

27. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

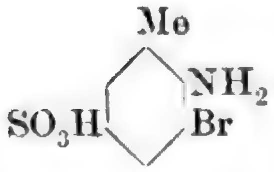
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

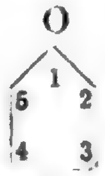


is 2 : 5-dibromobenzenesulphonic acid ;

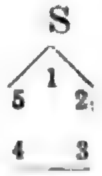


is 3-bromo-*o*-toluidine-5-sulphonic acid.

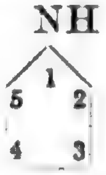
28. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (2nd edition, 1899, pp. 16—26) should be used, of which the following schemes may be regarded as typical :—



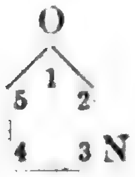
Furfuran.



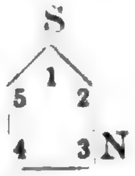
Thiophen.



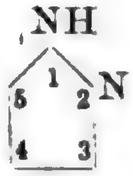
Pyrrole.



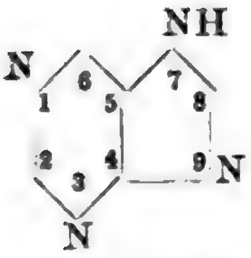
Oxazole.

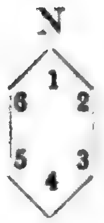


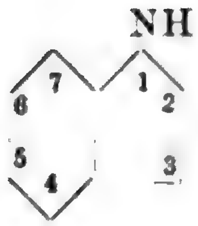
Thiazole.

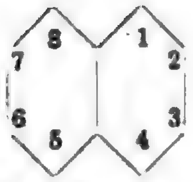


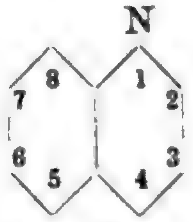
Pyrazole.

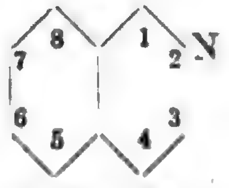

Purine.*

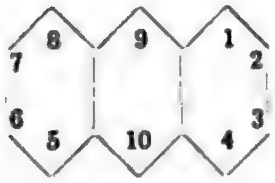

Pyridine.

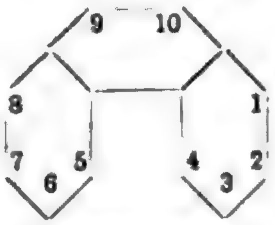

Indole.

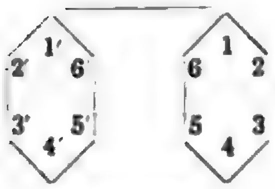

Naphthalene.

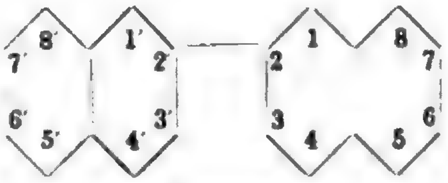

Quinoline.


*iso*Quinoline.


Anthracene.


Phenanthrene.


Diphenyl.


ββ-Dinaphthyl.

Manuscript.

29. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

30. Not more than one abstract must appear on a sheet.

31. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

32. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

33. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

34. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

⁂ The Editor's decision, in all matters connected with the Abstracts, must be considered final.

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* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page ; thus *Ber.* 1901, **34**, 2455 ; *Bull. Soc. chim.* 1901, [iii], **25**, 794 ; *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Agron.	Annales agronomiques.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path.	Beiträge für chemische Physiologie und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
* *Bied. Centr.*	Biedermann's Centralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bihang K. Svenska Vet.-Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Soc. chim.	Bulletin de la Société chimique de Paris.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Centr.*	Chemisches Centralblatt.
Chem. News	Chemical News.

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* Abstracts from the *Centralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Chem. Rev. Fett Harz Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Fed. Inst. Brewing.	Journal of the Federated Institutes of Brewing.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Milch Zeit.	Milch Zeitung.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Öfver K. Vet.-Akad. Förh.	Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch.	Pharmaceutical Archives.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften in München.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada.	Transactions of the Royal Society of Canada.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitth.	Tschermak's Mineralogische Mittheilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Farb. Text. Chem.	Zeitschrift für Farben- und Textil-Chemie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeit. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeit. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeit. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeit. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Tautomeric Atomic Groupings. By CONRAD LAAR (*Ber.*, 1901, **34**, 3516—3521).—A theoretical paper unsuitable for abstracting.
W. A. D.

Production of Ethylene from Inorganic Sources. By SAMUEL A. TUCKER and HERBERT R. MOODY (*J. Soc. Chem. Ind.*, 1901, **20**, 971—972).—Calcium carbide with water evolves only acetylene, and aluminium carbide gives methane. It was hoped that on treatment of a mixture of these carbides ethylene might be formed, but only acetylene and methane were found in the evolved gas. Barium silicide with water evolves hydrogen and if this be intimately mixed with barium carbide the hydrogen so formed acts on the acetylene and ethylene is produced. The mixture is obtained by heating in an electric furnace witherite, silica, and coke, and the gas produced by the action of water contains up to 15 per cent. of ethylene. On replacing the barium mixture by a corresponding strontium or calcium mixture, the proportion of ethylene formed sinks to 5 per cent. in the former case and 2 per cent. in the latter.
J. McC.

Reactions of Nitrosyl Chloride and Nitrosates. By WLADIMIR N. IPATIEFF and A. A. SOLONINA (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 496—501. Compare Abstr., 1900, i, 3 and 14).—From the results of previous experiments, Ipatieff concluded (*loc. cit.*) that unsaturated compounds containing either of the complexes $:C:CH\cdot$ or $:C:C:$ readily yield crystalline nitrosates and compounds with nitrosyl chloride, whilst with other unsaturated compounds possessing the structure $CH{:}CH_2$, $CH{:}CH$, or $C{:}CH_2$ this is not the case. It has, however, since been found by Prilejaeff that *iso*butylene, which contains the complex $C{:}CH_2$, also forms a crystalline product with nitrosyl chloride. This behaviour Ipatieff considers as probably due to the presence of two methyl groups, as in his own experiments with compounds containing this complex the carbon atom was combined with two different radicles. To obtain further information on this question, the authors have studied the behaviour of *iso*butylene, ψ-butylene, di*iso*butylene, δ-methylheptylene, and a hydrocarbon obtained from dipropylethylcarbinol.

On passing dry *iso*butylene into strongly cooled amyl nitrite and slowly adding concentrated hydrochloric acid to the solution, the *oxime* of *chloro*iso*butaldehyde*, $CMe_2Cl{:}NOH$, is obtained in crystals melting at 96—97°; on heating with sulphuric acid, it yields the chloroaldehyde which reduces Fehling's solution and ammoniacal silver oxide solution.

By the action of nitric acid on a solution of *iso*butylene in amyl nitrite and acetic acid, crystalline *iso*butylene nitrosate melting at 114—115° is obtained; when gently warmed with alcoholic potassium cyanide, it gives a *cyanide*, $CN{\cdot}CMe_2{\cdot}CH{:}NOH$, which melts at 92—93° and on hydrolysis yields an acid which was not investigated.

ψ-Butylene gives no crystalline nitrosate or compound with nitrosyl chloride.

δ-Methyl-γ-heptylene (1-methylpropyl-2-ethylethylene) yields a crystalline *compound* with nitrosyl chloride, $CMePr^{\alpha}Cl{\cdot}CEt{:}NOH$, melting at 61—62° and a crystalline *nitrosate*, $NO_3{\cdot}CMePr^{\alpha}{\cdot}CEt{:}NOH$, melting at 108—109°.

The hydrocarbon of the formula C_9H_{18}, obtained by acting on ethyldipropylcarbinol with bromine and reducing the dibromo-derivative thus formed by means of zinc dust and alcohol, and which must be either γ-propyl-β-hexylene or δ-ethyl-γ-heptylene, gives a crystalline *chloro-oxime*, $C_9H_{18}ONCl$, melting at 81—83° and a crystalline *nitrosate*, $C_9H_{18}O_4N_2$, melting at 92°.

T. H. P.

Transformation of Alcohols into Unsaturated Hydrocarbons by the Action of Oxalic Acid. By Nicolai D. Zelinsky and J. Zelikow (*Ber.*, 1901, 34, 3249—3256).—Pinacoline alcohol, when heated at 100—110° with anhydrous oxalic acid, yields a mixture of tetramethylethylene and another unsaturated hydrocarbon boiling at 65—67° and having a sp. gr. 0·6956 at 19°/4°. *cyclo*Hexanol and 3-methyl*cyclo*-1-hexanol, when heated with anhydrous or hydrated oxalic acid, furnish tetrahydrobenzene and methyl*cyclo*hexene respectively. Menthol under these conditions yields menthene. *r*-Borneol, when heated at 120—130° with hydrated oxalic acid, yields a hydrocarbon, $C_{10}H_{16}$, which becomes solid at 0°, melts at 3—4°, and boils at 155—160°; it has $[\alpha]_D$ 8·12°, and a sp. gr. 0·8622, and n_D 1·4656 at 25°. When this experiment is repeated with anhydrous oxalic acid, two terpenes are produced boiling respectively at 160—161° and 165—167°; these substances are inactive and do not solidify at 0°;

the isomeride of lower boiling point has a sp. gr. 0·8579, and n_D 1·4658 at 21°, the other hydrocarbon having a sp. gr. 0·8607 and n_D 1·4700 at 20°; the respective mol. refractions are 43·9 and 44·14, the calculated value in each case being 43·53.

l-Borneol, when heated at 120—130° with crystallised oxalic acid, yields an inactive terpene boiling at 156—157° under 750 mm. pressure; the product has a sp. gr. 0·8545 and n_D 1·4620 at 26°, the mol. refraction being 43·74.

The *hydrocarbon*, C_8H_{14}, derived from 1 : 3-dimethyl*cyclo*-3-hexanol boils at 126—127° under 750 mm. pressure and has a sp. gr. 0·8015 and n_D 1·4466 at 22° with a mol. refraction 36·61; it has $[\alpha]_D$ 95°.

The *hydrocarbon*, C_9H_{16}, obtained from 1-methyl-3-ethyl*cyclo*-3-hexanol boils at 147—150° under 743 mm. pressure; it has a sp. gr. 0·8087 and n_D 1·4514 at 25°, the mol. refraction being 41·3. The compound has $[\alpha]_D$ 56·8°.

The *hydrocarbon*, $C_{11}H_{20}$, produced from 1 : 3-dimethyl-4-*iso*propyl-*cyclo*-3-hexanol, boils at 180—182° under 753 mm. pressure and has $[\alpha]_D$ 88·53°; the sp. gr. and n_D at 26° are 0·8192 and 1·4561 respectively, the observed and calculated values of the mol. refraction being 50·43 and 50·24.

Methylfenchene, $C_{11}H_{18}$, prepared from methylfenchyl alcohol, $C_{11}H_{20}O$, boils at 172—173° under 743 mm. pressure, it has $[\alpha]_D$ 19·68°, a sp. gr. 0·8638 and n_D 1·4643 at 27°, the values of the observed and calculated mol. refraction being 47·97 and 48·14 respectively. This hydrocarbon is the first representative of the methylated terpenes having the general formula $C_{11}H_{18}$. G. T. M.

Pyrogenetic Reactions and Syntheses by means of the Electric Current. By WALTHER LÖB (*Zeit. Elektrochem.*, 1901, 7, 903—921).—When a wire is heated to redness by an electric current in the vapour of boiling chloroform, hydrochloric acid and tetrachloroethylene are the principal products of decomposition at comparatively low temperatures, hexachlorobenzene and hexachloroethane and chlorine appearing also at higher temperatures. The tetrachloroethylene is probably formed by polymerisation of dichloromethylene which is the primary product of the decomposition. This view is supported by the following observations. The gases evolved yield small quantities of carbon monoxide when passed through water. A mixture of chloroform and water vapour yields much carbon monoxide. A mixture of chloroform and aniline vapours yields triphenylguanidine.

Carbon tetrachloride, when treated in the same way, yields the same products as chloroform with the exception of hydrochloric acid. In admixture with other substances, it also exhibits the same behaviour, so that primary decomposition into dichloromethylene and chlorine is assumed. Tetrachloroethylene yields hexachlorobenzene as principal product and smaller quantities of hexachloroethane. The primary products appear, therefore, to be dichloroacetylene and chlorine, the former yielding hexachlorobenzene by polymerisation. Hexachloroethane yields tetrachloroethylene and chlorine. T. E.

Pyrogenetic Contact Reactions of Organic Compounds. By WLADIMIR N. IPATIEFF (*Ber.*, 1901, **34**, 3579—3589. Compare Abstr., 1901, i, 248).—When alcohol vapour is passed through a heated tube it decomposes mainly in two different ways, a portion being converted into ethylene and water, whilst the remainder forms aldehyde and hydrogen. A portion of the aldehyde then decomposes into carbon monoxide and methane, this decomposition being more complete as the temperature becomes higher. In a glass tube at 700°, very little decomposition occurs, but at 800—830°, about one-fifth of the alcohol decomposed is converted into ethylene and water, whilst four-fifths yield hydrogen and acetaldehyde. About one-third of the aldehyde is further decomposed into carbon monoxide and methane. In a platinum tube, a similar decomposition occurs, but at a lower temperature, about six-sevenths of the alcohol decomposed being converted into hydrogen and aldehyde, or the products of its decomposition. In presence of zinc, the decomposition occurs at a considerably lower temperature, the zinc remains unchanged, and the proportion of the ethylene decomposition to the aldehyde decomposition varies with the condition of the metal. When rods of zinc are used at 620—650°, very little ethylene is produced and the yield of aldehyde amounts to 80 per cent. of the alcohol decomposed, only a very small amount of secondary decomposition taking place. The amount of hydrogen formed is at the same time greatly increased. When zinc dust is employed at 550°, nearly half the alcohol is converted into ethylene and water and much of the latter is decomposed with evolution of hydrogen. Brass containing 33 per cent. of zinc gives a similar result to that obtained with zinc rods. A single experiment with ethyl ether passed over zinc at 750° also yielded ethylene, acetaldehyde, methane, and carbon monoxide, but the volume of methane is much greater than that of the carbon monoxide. Comparative experiments show that only metals which are easily oxidised and at the same time form easily reducible oxides, are capable of lowering the temperature of decomposition, and this may be explained by supposing that the primary action is decomposition into ethylene and water; the water then reacts with the metal forming free hydrogen and the metallic oxide, which is at once reduced by a second mol. of alcohol, water and acetaldehyde being formed. A. H.

Some New Derivatives of *sec.*-Butyl Alcohol. By JAMES F. NORRIS and ERIK H. GREEN [and, in part, B. R. RICKARDS and H. G. JOHNSON] (*Amer. Chem. J.*, 1901, **26**, 293—318).—The reduction of methyl ethyl ketone to *sec.*-butyl alcohol cannot be effected in acid or neutral solutions, but with alkaline reagents the alcohol is obtained in varying amounts. The best yields (in one case 74 per cent.) were obtained by the action of sodium on moist ethereal solutions, some dimethylpinacone being simultaneously produced. *sec.*-Butyl alcohol boils at 99·7—99·9° under 756 mm. pressure, has the sp. gr. 0·8078 at 20°/4° and 0·8226 at 0°/4°, and n_D 1·3949 at 25·3°. Attempts were made to resolve the alcohol into optically active substances by means of various micro-organisms, but without success. *sec.*-Butyl chloride, obtained by the action of hydrogen chloride on the alcohol in presence of zinc chloride, boils at 67·3—67·8°, has a sp. gr. 0·8707 at 20°/4°, and n_D 1·3953 at 25·2°. *sec.*-Butyl bromide, prepared by the action of phosphorus tribromide on the alcohol, boils at 91·3°, has a sp. gr. 1·2507 at 25°/4°, and n_D 1·4344 at 25·25°. *sec.*-Butyl acetate boils at 111·5—112° under 744 mm. pressure, has the sp. gr. 0·8648 at 25°/4° and 0·8900 at 0°/4°, and n_D 1·3866 at 25·3°. The *propionate* boils at 132—132·5°, has a sp. gr. 0·8657 at 20°/4°, and n_D 1·3938 at 25·19°. The iso*valerate* boils at 163—164° under 752 mm. pressure and has a sp. gr. 0·8482 at 20°/4°. *Di*-sec.-*butyl succinate* boils at 255·5—256·5° under 750 mm. pressure, has a sp. gr. 0·9735 at 20°/4°, and n_D 1·4238 at 25·25°. The *benzoate* boils at 234·5—235·5° under 757 mm. pressure and has a sp. gr. 0·9945 at 25°/4°.

Di-sec.-*butyl* (*dimethyl-γδ-hexane*), $CH_2Me\cdot CHMe\cdot CHMe\cdot CH_2Me$, obtained by the action of sodium on *sec.*-butyl bromide, is a fragrant, mobile liquid, which boils at 116—116·2° under 750 mm. pressure, has the sp. gr. 0·7332 at 0°/4° and 0·7165 at 25°/4°, and n_D 1·4038 at 25·2°. When it is heated with fuming nitric acid at 100°, a small quantity of a tertiary nitro-compound is produced.

Dimethylpinacone boils at 205—205·7° under 752 mm. pressure, has a sp. gr. 0·9529 at 25°/4°, and n_D 1·4521 at 25·25°, and when cooled solidifies to a mass of crystals melting at 49°; both liquid and solid are optically inactive. E. G.

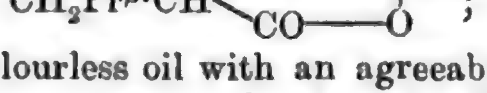
Dimethylpentadecylcarbinol and its Reaction with Bromine. By Wladimir N. Ipatieff and Grave (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 502—506).—In order to ascertain the influence of the mol. weight of an acid chloride on the yield of tertiary alcohol it gives when treated with an organo-zinc compound according to Butleroff's method, the authors have studied the action of zinc methyl (3 mols.) on palmityl chloride, $C_{15}H_{31}\cdot COCl$ (1 mol.). A good yield of the resulting *dimethylpentadecylcarbinol*, $OH\cdot CMe_2\cdot[CH_2]_{14}\cdot CH_3$, was obtained. After purification by crystallisation from ether, this substance melts at 34·5—35° and is soluble in alcohol or benzene; it is volatile in a current of steam only to a very small extent, and gives the normal mol. weight by the cryoscopic method. The action of bromine on the alcohol gives an almost theoretical yield of a *dibromo*-derivative, which has a sp. gr. 1·162 at 0°/0° and probably consists of a mixture of two isomerides, the main bulk being the compound having the formula $CMe_2Br\cdot CHBr\cdot[CH_2]_{13}\cdot CH_3$. By removing 1 mol. of hydrogen bromide from this dibromo-derivative, a liquid compound having a sp. gr. 0·922 at 0°/0° is obtained, whilst heating it with alcoholic potassium hydroxide yields a *hydrocarbon*, $C_{18}H_{34}$, boiling at 185—188°. The latter is a transparent, faintly smelling liquid which has a sp. gr. 0·845 at 0°/0° and decolorises bromine and potassium permanganate solutions; it is probably a trisubstituted allene of the constitution $CMe_2{:}C{:}CH\cdot C_{13}H_{27}$. T. H. P.

Condensation of Higher Alcohols: Tricapryl Alcohol. By Wladimir B. Markownikoff and P. Zuboff (*Ber.*, 1901, **34**, 3246—3249. Compare *J. Russ. Phys. Chem. Ges.*, 1889, **21**, 129; Abstr., 1901, i, 182).—Capryl alcohol (methylhexylcarbinol), when heated at

190° with powdered sodium hydroxide, undergoes condensation accompanied by the elimination of water. The chief product is formed in accordance with the equation $3C_8H_{18}O - 2H_2O = C_{24}H_{50}O$ and consists of a *secondary tricapryl alcohol*; this substance is a viscid, colourless liquid, lighter than water and boiling at 241—242° under 20 mm. and at 330° under the ordinary pressure; it yields a solid sodium derivative and when treated with valeryl chloride gives rise to a valerate. The compound seems to be alcoholic in character, for it readily condenses with phenylcarbimide, but does not interact with phenylhydrazine or ammoniacal silver nitrate; it is a saturated alcohol, and it only very slowly decolorises a chloroform solution of bromine. Small quantities of di- and tetra-capryl alcohols are produced during the condensation, the former of these compounds occurring in the oily fractions boiling at 220—225° under the ordinary pressure. G. T. M.

Dissociation of the Monatomic Alcohols, and their Ethers and Metallic Derivatives. By JOHN U. NEF (*Annalen*, 1901, **318**, 137—230. Compare Abstr., 1901, i, 626, and 1900, i, 4).—The alkylation of aniline by the sodium derivatives of the monohydric alcohols is explained by assuming that the latter substances undergo the alkylidene dissociation, $CHRR'\cdot ONa = NaOH + {>}CRR'$. The product always consists of the secondary amine and the yield is increased when aniline is replaced by its acetyl derivative. In this way, *iso*butyl- and *iso*amyl-aniline are readily obtained from the corresponding alkyloxides. When acetylethylaniline and the sodium derivative of an alcohol are heated in sealed tubes, ethylaniline and a substituted acetic acid are produced. The result is explained in the following manner. ${>}CRR' + CH_3\cdot CO\cdot NEtPh = CHRR'\cdot CH_2\cdot CO\cdot NEtPh$; $CHRR'\cdot CH_2\cdot CO\cdot NEtPh + NaOH = CHRR'\cdot CH_2\cdot CO_2Na + NHEtPh$. In this way, sodium ethoxide, *iso*butyloxide, and *iso*amyloxide give rise to *n*-butyric, γ-methylvaleric, and δ-methylhexoic acids respectively. The formation of similarly substituted fatty acids does not occur with the formyl, propionyl, and butyryl derivatives of ethylaniline.

The *sodium* salt of *β-hydroxymethyl-γ-methyl-α-*iso*butylvaleric acid* (*α-*iso*butyl-β-*iso*propyl-γ-hydroxybutyric acid; γ-hydroxyundecoic acid*), obtained by heating sodium *iso*amyl oxide with formylethylaniline at 150—160°, is accompanied by ethylaniline and *iso*amyl and decyl alcohols. The free acid is an oil which yields a crystalline *calcium* salt, $C_{22}H_{22}O_6Ca$; on distillation under diminished pressure, it loses water and passes into *α-*iso*butyl-β-*iso*propylbutyrolactone*,



$$CH_2Pr^{\beta}\cdot CH\left\langle\begin{matrix}CHPr^{\beta}\cdot CH_2\\ CO\text{———}O\end{matrix}\right.;$$

this substance is a colourless oil with an agreeable odour; it boils at 144—145° under 12 mm. pressure, has a sp. gr. 0·965 at 23° and does not solidify at 15°.

Iso*propyl*iso*butylsuccinic acid*, $CO_2H\cdot CHPr^{\beta}\cdot CH(CH_2Pr^{\beta})\cdot CO_2H$, results from the oxidation of the lactone with an alkaline solution of potassium permanganate; it crystallises from water in needles and melts at 142°.

*γ-Methyl-α-*iso*butylvaleric acid* (*α-*iso*butyl-β-*iso*propylbutyric acid;*

undecoic acid), $CHMePr^{\beta}\cdot CH(CH_2Pr_{\beta})\cdot CO_2H$, produced by reducing the lactone with fuming hydriodic acid and treating the impure iodoundecoic acid first produced with zinc dust and alcohol, is an oil boiling at 145° under 11 mm. pressure. The *chloride* boils at 99° under 13 mm. pressure and the *amide* melts at 82—83°.

*δ-Methyl-a-*iso*butylhexoic acid* (*a-*iso*butyl-β-*iso*amylacetic acid*), produced by the ethyl malonate synthesis, boils at 144—146° under 13 mm. pressure; the *chloride* boils at 100—102° under 15 mm. pressure. The *amide* crystallises in transparent needles melting at 84—85°; its melting point is depressed to 65—68° by the addition of the amide of the undecoic acid, the two acids are therefore isomeric, not identical.

The decyl alcohol obtained in the formylethylaniline condensation is identical with the substance described by Borodin and Guerbet (Abstr., 1899, i, 471, 472). The author, in repeating the latter investigator's experiments, finds that when *iso*amyl alcohol and sodium *iso*amyloxide are heated together in the absence of air the reaction does not commence below 300—330°, but that on passing dry air through the mixture condensation sets in at 150—170°, the products being the C_{10}-alcohol and valeric acid. This result is explained on the assumption that the initial phase of the reaction is the decomposition of the sodium derivative into sodium oxide, hydrogen, valeraldehyde, and the hypothetical *iso*amylidene, $CHMe_2\cdot CH_2\cdot CH<$. The unsaturated hydrocarbon then alkylates the valeraldehyde, forming a C_{10}-aldehyde, which is subsequently reduced to the decyl alcohol. The constitution of the decyl alcohol is determined by comparing the derivatives of the corresponding decoic acid with the analogous compounds of *iso*propyl*iso*amylacetic acid; they are found to be identical.

*δ-Methyl-a-*iso*propylhexoic* (iso*propyl*iso*amylacetic*) *acid*,

$$CH_2Pr^{\beta}\cdot CH_2\cdot CHPr^{\beta}\cdot CO_2H,$$

obtained from ethyl *iso*propyl*iso*amylmalonate (b. p. 138—145° under 14 mm. pressure), boils at 135—136° under 13 mm. pressure; the *chloride* boils at 87° under the same pressure; the *anilide* and *amide* crystallise in colourless needles melting respectively at 105° and 112°.

aγ-Decylglycol (*a-*iso*butyl-β-*iso*propyltrimethylene glycol*) [*ε-methyl-β-*iso*propyl-aγ-hexylene glycol*], $OH\cdot CH_2\cdot CHPr^{\beta}\cdot CH(CH_2Pr^{\beta})\cdot OH$, prepared by the action of powdered sodium hydroxide on valeraldehyde, boils at 146—150° under 30 mm. pressure and has a sp. gr. 0·92 at 23°; this substance is accompanied by valeric acid and the substituted acraldehyde, $C_{10}H_{18}O$. The glycol, valeraldehyde, or *iso*amyl alcohol, when heated at 280—300° with potash-lime, yields valeric acid and hydrogen.

Diisobutyl ketone, $CO(CH_2Pr^{\beta})_2$, results from the oxidation of valeraldehyde or the preceding glycol with chromic acid; it is an oil having an odour of peppermint and boiling at 56° under 11 mm. and at 164—166° under the ordinary pressure; the *oxime* is oily, boiling at 114—116° under 20 mm. pressure; the *semicarbazone* crystallises in needles and melts at 106—107°. Sodium *tert.*-amyloxide, when heated alone, yields methane, hydrogen, and a small quantity of γ-methyl-β-butylene; in the presence of potash-lime, it gives rise to methane, hydrogen, alkali carbonate and propionate, but not to amylene or any other olefine.

Benzophenone, when heated with sodium ethoxide, *iso*butyl oxide, or *iso*amyloxide, yields benzhydrol and in the case of the second experiment this product is accompanied by a small amount of *αα-dimethyl-ββ-diphenylpropionic acid*, $CHPh_2{\cdot}CMe_2{\cdot}CO_2H$; the acid crystallises in colourless plates and melts at 134—135°. This result is explained by supposing that diphenylmethylene, $Ph_2C<$ (an alkylidene derived from benzophenone) combines with *iso*butyric acid.

A large portion of the communication is devoted to the decompositions occurring when the alcohols, ethers, aldehydes, and fatty acids are heated; these reactions are explained by assuming that the initial dissociations involve the production of alkylidenes. This part of the investigation cannot, however, be satisfactorily summarised.

G. T. M.

Oxidation of Propylene Glycol by Oxidising Ferments. By André Kling (*Bull. Soc. Chim.*, 1901, [iii], **25**, 905—910).—Details of work already published (Abstr., 1901, i, 625). N. L.

Structure of *iso*Butylene Chlorohydrin. By K. Krassusky (*J. pr. Chem.*, 1901, [ii], **64**, 387—393).—A claim for priority (see Abstr., 1901, i, 246; Michael, *ibid.*, 625). R. H. P.

Action of Mannitol on Bismuth Nitrate. By Ludwig Vanino and Otto Hauser (*Zeit. anorg. Chem.*, 1901, **28**, 210—218).—Bismuth nitrate dissolves to a clear solution in an aqueous solution of mannitol and these solutions are more stable the greater the proportion of mannitol. When molecular proportions of bismuth nitrate and mannitol are employed, the compound $BiO{\cdot}NO_3,C_6H_{14}O_6$ is obtained by adding alcohol and, after separating the mannitol which is precipitated, adding ether. It is sparingly soluble in water and easily so in potassium or sodium hydroxide.

The *compound*, $Bi_2O_3,2C_6H_{14}O_6$, is obtained by allowing a solution of bismuth nitrate in mannitol to remain more than three months and then precipitating it with alcohol. It separates in yellowish-white, crystalline granules, is slightly soluble in water, easily so in potassium or sodium hydroxide, but insoluble in ammonia and barium hydroxide solution and is partially decomposed when dissolved in water.

The *compound*, $Bi_2O_3,4C_6H_{14}O_6,3H_2O$, crystallises from the filtrate obtained in the precipitation of the preceding compound, is a white powder easily soluble in water, has not the sweet taste of mannitol, and gradually decomposes on exposure to the air. When heated at 130°, it is converted into the compound $Bi_2O_3,4C_6H_{14}O_6$, which is insoluble in water and easily soluble in potassium or sodium hydroxide.

The solution of bismuth nitrate in mannitol, since it contains no excess of acid, is very suitable for the preparation of bismuth salts by double decomposition. The authors have prepared the following salts from this solution, bismuth oxalate, citrate, gallate, salicylate, camphorate: the double salts with potassium chromate and dichromate, the tri-iodide, and a white, amorphous precipitate with borax.

E. C. R.

Action of Zinc Methyl on Alcohols. By S. A. TOLKATSCHEFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 469—474).—*Zinc ethoxide*, $Zn(OEt)_2$, is obtained, together with methane, as a white powder by the action of zinc methyl on ethyl alcohol in an atmosphere of carbon dioxide or, better, of nitrogen or hydrogen. The crude product contains a little zinc methyl ethoxide, from which it may be freed by heating with excess of ethyl alcohol. The ethoxide cannot be distilled, is insoluble in ordinary solvents, and readily absorbs moisture from the air.

Zinc iso*butyloxide*, $Zn(O{\cdot}CH_2{\cdot}CHMe_2)_2$, prepared from zinc methyl and *iso*butyl alcohol, is a fine, white powder which is insoluble in the ordinary solvents. It cannot be distilled, and when heated it decomposes, the volatile products being mainly *iso*butylene, hydrogen, and *iso*butyl *iso*butyrate with smaller quantities of carbon monoxide and dioxide, saturated hydrocarbons, *iso*butaldehyde, and *iso*butyl alcohol; no *iso*butyl ether is obtained. A residue of 44 per cent. of the *iso*butyloxide remains in the distilling flask as a porous, grey mass.

T. H. P.

Glycerophosphorous Acid and Glycerophosphites. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and F. PERRIN (*Compt rend.*, 1901, **133**, 643—644).—When phosphorus trichloride is slowly added to excess of cooled glycerol, hydrogen chloride is eliminated and a syrup obtained which contains the excess of glycerol, hydrochloric acid, and *glycerophosphorous acid*, $PHO(OH){\cdot}OC_3H_5(OH)_2$. The *calcium* salt is obtained by dissolving the syrup in water, removing hydrogen chloride by moist silver oxide, and neutralising with calcium carbonate. After evaporation, addition of alcohol precipitates the salt as a white, crystalline, deliquescent powder. In aqueous solution, the acid rapidly hydrolyses, forming glycerol and phosphorous acid. Its salts, with the exception of the silver salt, are very soluble in water; the alkali salts are also soluble in alcohol.

K. J. P. O.

Reducing Action of certain Nitro-derivatives. By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1901, **133**, 540—542).—Methyl and ethyl nitrates and glycerol dinitrate and trinitrate have no reducing action on alkaline solutions of cupric salts. Erythritol tetranitrate has a slight reducing action and dulcitol hexanitrate a strong reducing action similar to that of the mannitol derivatives (compare Abstr., 1901, i, 662).

C. H. B.

Nitro-derivative of Pentaerythritol. By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1901, **133**, 590—592).—Pentaerythritol, when treated with fuming nitric acid and sulphuric acid, yields a *tetranitropentaerythritol* which forms colourless prisms melting at 138—140°, deflagrating if suddenly heated and detonating under a hammer. It is not affected by ordinary reducing agents and has no action on alkaline solutions of cupric salts, differing in this respect from erythritol tetranitrate (compare preceding abstract).

C. H. B.

(Derived) Nitrates of Arabitol and Rhamnitol. Constitution of certain Ethereal Nitrates. By LÉO VIGNON and F. GERIN (*Compt. rend.*, 1901, **133**, 641—643. Compare preceding abstract).—*Arabitol penta-*

nitrate, $C_5H_7(NO_3)_5$, is prepared by treating arabitol with fuming nitric acid at $-5°$, and precipitating the nitrate with sulphuric acid, and is obtained as a colourless, non-crystallisable syrup, which readily reduces alkaline cupric solutions. *Rhamnitol pentanitrate*, $C_6H_9(NO_3)_5$, is a syrup, also possessing energetic reducing properties. The view is expressed that the reducing properties are due to an oxidation of the primary alcohol group, $\cdot CH_2\cdot OH$, into the group $\cdot CH(OH)_2$; the latter is then converted by nitrous acid into the group $\cdot CH(OH)\cdot ONO$, which, under the influence of alkalis, yields aldehyde and nitrite, $\cdot CH(OH)\cdot ONO + KOH = KNO_2 + H_2O + \cdot CHO$, and thus reduces Fehling's solution. The oxidation of the primary alcohol group only occurs when at least two $\cdot CH\cdot NO_3$ groups are present in the molecule. K. J. P. O.

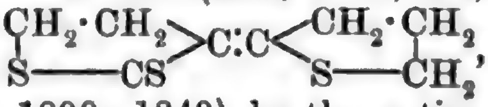
Product of Condensation of Butyric Acid. By GIACOMO ALBO (*Arch. Sci. phys. nat. Genève*, 1901, [iv], **12**, 339—346).—On distilling commercial butyric acid, a fraction, boiling at 158—160°, was obtained which, when kept for two months exposed to light, deposited a white, gelatinous solid. This *substance*, $C_{18}H_{22}O_8$, is a tribasic acid, which was only obtained as an amorphous powder melting at 220°. The *silver* salt, $C_{13}H_{19}O_8Ag_3$, prepared from an ammoniacal solution of the acid and silver nitrate, is amorphous; a green *copper* salt and a *barium* salt were also prepared. K. J. P. O.

Action of Zinc on a Mixture of Ethyl Acetoacetate with Methyl or Ethyl Iodide. By SERGIUS N. REFORMATSKY and N. LUKASCHEWITSCH (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 436—447).—The action of zinc and ethyl acetoacetate on either methyl or ethyl iodide yields a crystalline compound of the composition $C_{12}H_{19}O_6IZn$; with the former iodide, the gaseous product consists of methane with a small proportion of hydrogen, whilst in the case of ethyl iodide, ethane and hydrogen are evolved. The author considers all the possible formulæ for the crystalline compound mentioned, and comes to the conclusion that it has the structure $IZnO\cdot CMe{:}CH\cdot CO_2Et,C_6H_{10}O_3$. The reaction takes place in the following three stages: (1) $Zn + MeI = ZnMeI$, (2) $OH\cdot CMe{:}CH\cdot CO_2Et + ZnMeI = IZnO\cdot CMe{:}CH\cdot CO_2Et + CH_4$, (3) $IZnO\cdot CMe{:}CH\cdot CO_2Et + C_6H_{10}O_3 =$

$$IZnO\cdot CMe{:}CH\cdot CO_2Et,C_6H_{10}O_3.$$

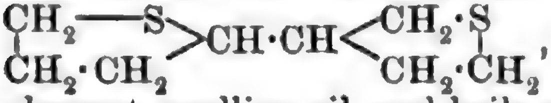
On passing dry ammonia through a cooled ethereal solution of this compound, a white, microcrystalline precipitate of the formula $C_9H_{38}O_3N_7I_4Zn_3$ separates out; it is insoluble in organic solvents, but is dissolved and decomposed by mineral acids. No definite product could be obtained with aniline or phenylhydrazine. T. H. P.

Trithiodibutyrolactone. By FRITZ WEIGERT (*Ber.*, 1901, **34**, 3386—3405).—Trithiodibutyrolactone,



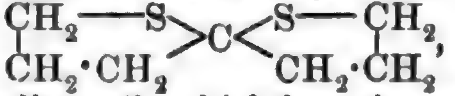
$$\begin{matrix}CH_2\cdot CH_2\\|\qquad\quad\\S\text{——}CS\end{matrix}\!\!>C{:}C<\!\!\begin{matrix}CH_2\cdot CH_2\\\qquad\quad|\\S\text{——}CH_2\end{matrix},$$

was prepared by Gabriel and Day (Abstr., 1890, 1249) by the action of alcoholic potassium hydrogen sulphide on γ-chlorobutyronitrile, and crystallises in large, red tablets of the triclinic system [$a:b:c = 0.736921:1:0.803146$; $\alpha = 125°23'40''$; $\beta = 95°5'16''$; $\gamma = 93°15'52''$]. It melts at 116° and does not decompose at 180°. It unites with chlorine and bromine, forming unstable compounds, and with iodine gives a *derivative*, $C_8H_{10}I_2S_3$, which separates out as a dark red, crystalline powder and melts and decomposes at 136°. With bromoacetic acid, it yields a thetine *derivative*, $C_8H_{10}S_3,CH_2Br\cdot CO_2H$, which crystallises in small, yellow needles melting at 154·5—155°. Trithiodibutyrolactone yields a *hydrazone*, $C_8H_{10}S_2{:}N_2H_2$, which forms large crystals melting at 104·5°, and also an *oxime*, $C_8H_{10}S_2{:}NOH$, which crystallises in stellate groups of needles or rhombohedral tablets, sinters at 197° and melts and decomposes at 201—202°. On reduction, the thiolactone is converted into *bistetramethylene sulphide*,



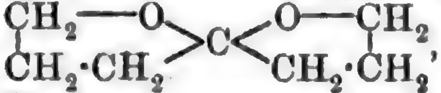
$\begin{matrix}CH_2—S\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CH{<}\begin{matrix}CH_2\cdot S\\ CH_2\cdot CH_2\end{matrix}$, which is a light yellow, viscid, unpleasant smelling oil, and boils at 300·7°. The corresponding *sulphone*, $C_8H_{14}O_4S_2$, crystallises in six-sided tablets melting at 145—146°.

When boiled with baryta water, the thiolactone yields a *mercaptothionic acid*, $OH\cdot C_8H_{10}S_2\cdot SH$, which, however, very readily loses water and reforms the original compound. The dibenzoyl derivative, *mercaptothiondibenzoic anhydride*, $C_{22}H_{20}O_3S_3$, crystallises in colourless plates melting at 91—92°. When the crude mercaptothionic acid is heated with dilute sulphuric acid, *sulphetone*,



$$\begin{matrix}CH_2—S\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}S—CH_2\\ CH_2\cdot CH_2\end{matrix},$$

is formed as a light yellow oil which has the sp. gr. 1·1557 at 17·5°, and boils at 230—260°. It does not react with hydrazine or hydroxylamine and is not affected by reducing agents. On oxidation, it yields *sulphonetone*, $C_7H_{12}O_4S_2$, which crystallises in rhombohedral forms, melts at 164°, and can be sublimed. Sulphetone appears to be the sulphur analogue of the oxetone,



$\begin{matrix}CH_2—O\\ CH_2\cdot CH_2\end{matrix}{>}C{<}\begin{matrix}O—CH_2\\ CH_2\cdot CH_2\end{matrix}$, of Fittig and Ström (*Annalen*, 1890, **256**, 57), and it is from the formation of this compound that the constitution of the trithiodibutyrolactone has been deduced.

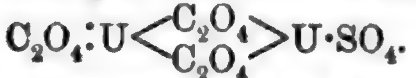
The thiolactone is converted by hydrogen peroxide into a *compound*, $C_8H_{10}OS_3$, which crystallises in orange-yellow needles melting at 134·5°. Benzoyl chloride converts the thiolactone into a *compound*, $C_{15}H_{13}ClS_3$, which crystallises in matted, lemon-yellow, hygroscopic needles melting at 227°. This substance behaves as the chloride of a base, and other salts can be prepared from it, although the free base has not been isolated. The *platinichloride*, $(C_{15}H_{13}ClS_3)_2PtCl_4$, forms yellow needles; the *nitrate* melts at 218°; the *bromide* crystallises in needles, and melts and decomposes at 267°; the *iodide* melts at 275°; and the *thiocyanate* melts and decomposes at 212°. *p*-Nitrobenzoyl chloride yields an analogous *derivative*, $NO_2\cdot C_6H_4\cdot C_9H_8ClS_3$, which melts at 210°, and forms an *iodide* melting at 242°. Acetyl chloride also appears to act in a similar manner, but the chloride has not been obtained pure. The *thiocyanate*, $C_{10}H_{11}S_3\cdot SCN$, crystallises in slender needles and melts at 175°.

A. H.

Oxalouranous Compounds. By Volkmar Kohlschütter (*Ber.*, 1901, **34**, 3619—3635. Compare Abstr., 1901, i, 448).—Uranous oxalate, $U_2(C_2O_4)_4$ (*loc. cit.*), yields an *acid oxalate*, $U_2(C_2O_4)_2,H_2C_2O_4,8H_2O$, in the form of a white powder, which is readily converted back into the green compound on treatment with water or dilute acids.

Trioxalodiuranous chloride, $U_2(C_2O_4)_3Cl_2,12H_2O$, obtained when uranous oxalate is dissolved in concentrated hydrochloric acid and the solution kept over sulphuric acid, forms glistening, colourless needles which turn pink when heated at 100°. All the uranium is not deposited from the solution in the form of the chloride, and if the crystals are kept too long in contact with the mother liquor they redissolve. Water decomposes the chloride, hydrogen chloride being liberated.

A *sulphate*, $U_2(C_2O_4)_3SO_4,12H_2O$, obtained when the solution of the chloride is cooled and treated with dilute sulphuric acid, forms greyish-green, minute needles, and cannot be obtained by treating the chloride with sulphuric acid. It is suggested that the chloride and sulphate belong to two distinct isomeric series, for example, $C_2O_4(U{\cdot}C_2O_4{\cdot}Cl)_2$ and



$C_2O_4{:}U{<}\genfrac{}{}{0pt}{}{C_2O_4}{C_2O_4}{>}U{\cdot}SO_4$.

Oxalouranous sulphate, $U_2C_2O_4(SO_4)_2,6H_2O$, is formed when uranous oxalate is boiled with dilute sulphuric acid, and crystallises in dark olive-green, flat prisms. When the urano-oxalate is dissolved in concentrated sulphuric acid, it yields *uranous sulphate*, $U(SO_4)_2,4H_2O$, a colourless powder readily decomposed by water; a *sulphate*, $U(SO_4)_2,2H_2O$, has also been obtained in the form of grey needles. Diuranous sulphate, $U_2(SO_4)_4,8H_2O$, is formed when a solution of the compound, $U(SO_4)_2,4H_2O$, in dilute sulphuric acid is evaporated, and is identical with Hillebrand and Melville's sulphate. *Potassium uranous sulphate*, $U(SO_4)_2,K_2SO_4,2H_2O$, crystallises in glistening, green plates. *Ammonium uranous sulphate*, $U(SO_4)_2,4(NH_4)_2SO_4,3H_2O$, forms deep green, glistening pyramids. *Potassium uranotetraoxalate*, $U_2(C_2O_4)_4(C_2O_4)_4K_8,10H_2O$, obtained by precipitating a solution of urano-oxalate in potassium oxalate with alcohol, is a colourless, minutely crystalline compound, and its solution is not oxidised on evaporation.

The *barium* salt, $U_2(C_2O_4)_4(C_2O_4)_4Ba_4,12H_2O$, forms reddish-violet needles, and when warmed at 105° turns green. *Potassium diuranoheptaoxalate*, $U_2(C_2O_4)_4(C_2O_4)_3K_6,8H_2O$, crystallises in green prisms. *Potassium diuranopentaoxalate*, $U_2(C_2O_4)_4,K_2C_2O_4,8H_2O$, is a greyish-green, crystalline powder. Oxalothorium chloride, $Th_2(C_2O_4)_3Cl_2,9H_2O$, obtained by the action of concentrated hydrochloric acid on thorium oxalate, crystallises in flat prisms, and is decomposed when boiled with water. The action of various salts, alkali carbonates, sulphates, and arsenates on uranous oxalate has been studied. The relationship between the colour and constitution of the urano-oxalates is also discussed. J. J. S.

Formation of Carbon Rings. By A. Kötz and P. Speiss (*J. pr. Chem.*, 1901, [ii], 64, 394—400).—A preliminary account of researches on the formation of carbon rings by the action of dihaloids on disodium derivatives of the esters of methylene- and other dicarboxylic acids.

The action of methylene di-iodide on ethyl ethanetetracarboxylate yields a colourless *oil*, $C_{15}H_{22}O_8$, which boils at 155—160° under 12 mm. pressure and is not identical with the ester obtained by Perkin by the action of iodine on ethyl disodiomethylenedimalonate. The ethylene dihaloids have no action on ethyl disodioethanetetracarboxylate, but trimethylene dibromide interacts with it, forming ethyl *cyclo*pentanetetracarboxylate. R. H. P.

Bromomalonic Dialdehyde. By ROBERT LESPIEAU (*Compt. rend.*, 1901, **133**, 538—540).—The compound, $C_3H_3O_2Br$, obtained by the action of excess of bromine on many compounds containing C_3, such as dibromoallyl methoxide, $CHBr\!:\!CBr\cdot CH_2\cdot OMe$, or bromoallyl alcohol, $CHBr\!:\!CH\cdot CH_2\cdot OH$, or its methyl ester, is *bromomalonic dialdehyde*; it melts and decomposes at 140°, is very soluble in water or organic solvents, and can be crystallised from benzene. Its aqueous solution yields a reddish-violet coloration with ferric chloride, a green precipitate with cupric acetate, a violet coloration with Fischer's reagent, and a coloration with magenta decolorised by sulphurous acid. With potassium carbonate, it yields a crystalline derivative, $CKBr(CHO)_2$, and with phenylhydrazine it forms Balbiano's 1-phenyl-4-bromopyrazole. C. H. B.

Interaction of Formaldehyde and Acetonylacetone. By LUDWIG KNORR and PAUL RABE (*Ber.*, 1901, **34**, 3489—3490).—Formaldehyde interacts with acetonylacetone in dilute alkaline solution, yielding about 14 per cent. of a heavy *oil*, $C_8H_{10}O_2$, boiling at 200—201°, which slowly deposits crystals of the same composition melting at 32°. The oil instantaneously decolorises bromine and is more rapidly attacked than acetonylacetone by alkaline potassium permanganate; it combines with phenylhydrazine at 140—150°, giving a *derivative*, $C_{14}H_{16}ON_2$, which boils at 220—225° under 30 mm. pressure. W. A. D.

The Oxycelluloses. By A. NASTUKOFF (*Ber.*, 1901, **34**, 3589—3591. Compare Abstr., 1901, i, 315).—Cellulose yields 90 per cent. of β-oxycellulose when it is heated for an hour on the water-bath with about 2·5 parts of nitric acid of sp. gr. 1·3. This fact destroys the value of the theory of the constitution of cellulose founded by Cross and Bevan (Trans., 1883, **43**, 22) on their observation that only 30 per cent. of β-oxycellulose could be obtained from cellulose.

The barium salt of β-oxycellulose contains, according to two analyses, 4·9 and 5·8 per cent. of barium, corresponding with the mol. weights 1353 and 1104, on the assumption that the substance is a monobasic acid. The barium salt of γ-oxycellulose, on the other hand, only contains about 1 per cent. of barium, corresponding with a molecular weight of nearly 7000. The salts of the β-oxycelluloses are hard, whilst those of the γ-oxycelluloses are brittle; they also differ in their behaviour when heated and when their solutions are evaporated. A. H.

Dimethylethanolamine. By LUDWIG KNORR and HERMANN MATTHES (*Ber.*, 1901, **34**, 3482—3484).—Ethylene oxide readily combines completely at the ordinary temperature with dimethylamine in presence of a little water to form dimethylethanolamine [dimethylhydroxyethylamine] (compare Abstr., 1899, i, 461); to prepare the latter, however, in the anhydrous state, it is necessary to heat the dry ingredients for 40 hours at 150°. Thus obtained, it boils at 13·5° (corr.) under 758 mm. pressure, has a sp. gr. 0·8866 at 20°/4°, μ_D 1·430 at 20°, and a mol. refraction 25·93 (calc. 26·08). The *picrate* (with $\frac{1}{2}H_2O$) crystallises in stout needles and when dry melts at 96—97°; the *picrolonate* crystallises from dilute alcohol in yellow needles and melts and decomposes at 197°. W. A. D.

Ethyl Bromo- and Chloro-aminocrotonates. By ROBERT BEHREND and HERMANN SCHREIBER (*Annalen*, 1901, **318**, 371—381. Compare Abstr., 1900, i, 210).—This is chiefly an account of work already published. Hofmann's process for the preparation of acetylbromoamide does not give a very good yield of this product, but when acetamide is dissolved in well cooled bromine and the mixture treated with a concentrated solution of potassium hydroxide (1 : 1), 40—55 per cent. of the theoretical amount is obtained. G. T. M.

Double Salts of Bismuth Thiocyanate and Potassium Thiocyanate. By LUDWIG VANINO and OTTO HAUSER (*Zeit. anorg. Chem.*, 1901, **28**, 219—222).—The *double* salt, $Bi(SCN)_3,3KSCN$, is obtained by adding the calculated quantity of potassium thiocyanate to a solution of bismuth nitrate in mannitol and then precipitating the mannitol and potassium nitrate with alcohol and allowing the filtrate to crystallise at the ordinary temperature. It separates from alcohol in red crystals, is not hygroscopic, does not change on exposure to the air, and is decomposed by water into a yellowish, amorphous powder.

The *double* salt, $Bi(SCN)_3,9KSCN$, is obtained in a similar manner to the preceding salt, a larger proportion of potassium thiocyanate being used; it crystallises in large, deep red crystals, is exceedingly hygroscopic, and decomposes at the ordinary temperature into a red compound mixed with sulphur and bismuth sulphide.

The ammonium double salts are obtained in the same manner, but cannot be purified. E. C. R.

The so-called *iso*Amides and True Amides. By KARL AUWERS (*Ber.*, 1901, **34**, 3558—3559).—Polemical; a reply to Hantzsch and Voegelen (Abstr., 1901, i, 676). T. M. L.

Action of Urethane on Pyruvic Acid. By L. J. SIMON (*Compt. rend.*, 1901, **133**, 535—538).—The direct action of urethane (ethyl carbamate) on pyruvic acid in the absence of any condensing agent yields *diurethanepyruvic acid*, $CMe(NH\cdot CO_2Et)_2\cdot CO_2H$, a white, crystalline solid, which melts at 138—139°, readily remains in a state of superfusion, and decomposes before it volatilises. It is only slightly soluble in cold water and is hydrolysed in hot water, but dissolves in most organic solvents. It is a somewhat strong acid and can be titrated with either phenolphthalein or methyl-orange as indicator; the potassium and silver salts are crystallisable, and the zinc, barium, lead, and mercurous salts are soluble, but the mercuric and ferric salts are insoluble in water.

Ethyl diurethanepyruvate, obtained in the usual way from the acid or by the action of ethyl carbamate on ethyl pyruvate in presence of hydrochloric acid, forms slender, white needles, which melt at 109° and can be recrystallised from boiling water. Diurethanepyruvic acid has none of the properties characteristic of ketones and does not give the pyruvic acid reaction with sodium nitroprusside; when boiled with water, it readily yields pyruvic acid and ethyl carbamate.

C. H. B.

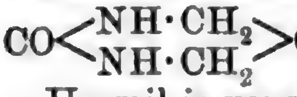
Action of Carbamide on Pyruvic Acid. By L. J. Simon (*Compt. rend.*, 1901, **133**, 587—590).—In the production of homoallantoin by the action of carbamide on pyruvic acid as described by Grimaux, the first product of the reaction is *homoallantoic acid*,

$$CO_2H\cdot CMe\cdot(NH\cdot CO\cdot NH_2)_2,$$

which is readily obtained by the interaction of carbamide and pyruvic acid in the calculated proportion at the ordinary temperature in presence of water or alcohol. It is a white, microcrystalline solid, which begins to decompose at 140° without melting; it can be titrated with ordinary indicators, forms a crystallisable potassium salt, the aqueous solution of which yields no precipitates with solutions of metallic salts. The ethyl ester is crystalline and decomposes at 195—200° without melting. When heated for a long time with a small quantity of water, homoallantoic acid is almost completely converted into homoallantoin (pyruvil). The behaviour of carbamide with pyruvic acid is similar to that of urethane (preceding abstract).

Semicarbazide and pyruvic acid yield compounds analogous to the hydrazines. The ester, $CO_2Et\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2$, is a white, crystalline compound, which melts and begins to decompose at 204—205°; it has been obtained in a different manner by Thiele and Bailey (Abstr., 1899, i, 169). The corresponding acid decomposes without melting at about 200°. C. H. B.

Electrolytic Reduction of Cyclic Ureides. By Julius Tafel and Ludwig Reindl (*Ber.*, 1901, **34**, 3286—3291).—The electrolytic reduction of parabanic acid dissolved in 60—70 per cent. sulphuric acid yields a mixture of hydantoin and ethylenecarbamide, and that of dialuric acid affords hydrouracil, together with trimethylenecarbamide and a small quantity of a *substance*, $C_4H_8O_2N_2$, possibly



$CO\left<\begin{matrix}NH\cdot CH_2\\NH\cdot CH_2\end{matrix}\right>CH\cdot OH$, melting between 185° and 195°.

Uramil is very susceptible to reduction, but yields principally amorphous products and only a small quantity of hydrouracil; alloxan also yields only a small proportion of hydrouracil together with some alloxantin and a large amount of non-crystalline material. W. A. D.

Oxidation of Benzene Hydrocarbons by means of Manganese Dioxide and Sulphuric Acid. By H. Fournier (*Compt. rend.*, 1901, **133**, 634—636).—When oxidised in the cold with manganese dioxide and sulphuric acid (sp. gr. = 1·53), *o*-xylene yields *o*-tolualdehyde, representing 37 per cent. of the calculated amount. ψ-Cumene is oxidised to the extent of 22 per cent. to *o*-xylaldehyde. Cymene yields only a small quantity of cuminaldehyde; ethylbenzene gives benzaldehyde and acetophenone (methyl phenyl ketone).

K. J. P. O.

Digitized

Action of Sodium Nitrite on 1-Chloro-2 : 4-dinitrobenzene and Picryl Chloride. By OTTO KYM (*Ber.*, 1901, **34**, 3311—3313).—1-Chloro-2 : 4-dinitrobenzene is converted quantitatively by sodium nitrite in dilute alcoholic solution at the ordinary temperature into sodium 2 : 4-dinitrophenoxide ; the compound, $C_6H_4(NO_2)_2\cdot ONO$, is probably the initial product, but could not be isolated. Nitrogen trioxide is without action on 1-chloro-2 : 4-dinitrobenzene in cold ethereal solution.

Sodium nitrite converts picryl chloride in cold acetone instantaneously into sodium picrate, but does not act on either *o*- or *p*-chloronitrobenzene. W. A. D.

Preparation from *p*-Nitroaniline of Tri-, Tetra-, and Penta-iodobenzene and Allied Compounds. By CONRAD WILLGERODT and EMIL ARNOLD (*Ber.*, 1901, **34**, 3343—3354).—1 : 3 : 5-*Di-iodonitrobenzene*, $C_6H_3I_2\cdot NO_2$, prepared by boiling diazotised 2 : 6-di-iodo-4-nitroaniline with alcohol, crystallises from alcohol in yellow needles and melts at 95—96°. 3 : 5-*Di-iodoaniline*, $C_6H_3I_2\cdot NH_2$, crystallises in transparent needles and melts at 105° ; the *sulphate* forms glistening, white flakes melting at above 200° with liberation of iodine, the *hydrochloride*, white needles decomposing without melting at above 200°, the *platinichloride*, yellow needles, and the *acetyl* derivative, small white needles melting at 101—102°. 1 : 3 : 5-Tri-iodobenzene, $C_6H_3I_3$, prepared from di-iodoaniline, crystallises from acetic acid in long, flexible needles, melts at 180°, and is identical with that prepared by Baeyer from iodoacetylene, and by Istrati.

1 : 2 : 3-*Tri-iodo-5-nitrobenzene*, $C_6H_2I_3\cdot NO_2$, prepared from 2 : 6-di-iodo-4-nitroaniline, crystallises from alcohol in yellow needles, and melts at 105°. 3 : 4 : 5-*Tri-iodoaniline*, $C_6H_2I_3\cdot NH_2$, crystallises from ether in white needles, melts at 78°, and can be distilled in a current of steam ; the *sulphate* crystallises in white flakes and melts with decomposition when heated ; the *hydrochloride* forms small needles and melts with decomposition when heated ; the *platinichloride* forms reddish needles ; the *acetyl* derivative crystallises in needles, and melts at 135°.

5 : 7-*Di-iodoquinoline*, $C_9NH_5I_2$, prepared by Skraup's method from 3 : 5-di-iodoaniline, crystallises from alcohol in white needles, sublimes when heated, and melts at 132° ; the *methiodide* and *methochloride* melt with decomposition at above 250°.

5 : 6 : 7-*Tri-iodoquinoline*, $C_9NH_4I_3$, prepared from 3 : 4 : 5-tri-iodoaniline, crystallises from alcohol in white needles and melts at 102°.

1 : 2 : 3-*Tri-iodobenzene*, $C_6H_3I_3$, prepared from 3 : 4 : 5-tri-iodoaniline, crystallises from alcohol in white needles and melts at 86° ; it is possibly identical with a tri-iodobenzene melting at 83—84° described by Istrati.

1 : 2 : 4 : 6-*Tetraiodobenzene*, $C_6H_2I_4$, crystallises from acetic acid or ether and melts at 148°.

2 : 6-*Di-iodo*-1 : 4-*diaminobenzene*, $C_6H_2I_2(NH_2)_2$, crystallises from hot water in needles, melts at 108°, and is readily oxidised to di-iodoquinone.

2 : 3 : 4 : 6-*Tetraiodo*-1 : 4-*diaminobenzene*, $C_6I_4(NH_2)_2$, prepared by the action of iodine chloride on the preceding compound, melts at 152°.

1 : 2 : 4 : 5 *Tetraiodobenzene*, $C_6H_2I_4$, prepared from the preceding

compound, crystallises from ether in white needles, sublimes when heated, and melts at 165°.

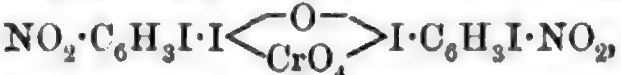
2 : 3 : 4 : 5-*Tetraiodoaniline*, $C_6HI_4 \cdot NH_2$, prepared by the action of iodine chloride on 3 : 4 : 5-tri-iodoaniline, crystallises from alcohol in needles, melts at 92°, and becomes violet under the influence of light. 1 : 2 : 3 : 4-*Tetraiodobenzene*, $C_6H_2I_4$, crystallises from alcohol, sublimes when heated, and melts at 114°. Istrati has described two tetraiodobenzenes melting at 220° and 247°, whilst the three compounds now described melt at 148°, 165°, and 114°; as only three tetraiodobenzenes are possible, there must be an error awaiting discovery.

Pentaiodobenzene, C_6HI_5, from 2 : 3 : 4 : 5-tetraiodoaniline, forms white needles, crystallises from alcohol, sublimes when heated, and melts at 172°. T. M. L.

Derivatives of Symmetrical Di-iodonitrobenzene containing Polyvalent Iodine. By CONRAD WILLGERODT and WALDEMAR ERNST (*Ber.*, 1901, **34**, 3406—3416).—1-*Iodo-3-nitrophenyl 5-iodochloride*, $NO_2 \cdot C_6H_3I \cdot ICl_2$, obtained by passing chlorine into a warm (30°) acetic acid solution of *s*-di-iodonitrobenzene to which a little chloroform has been added, forms small, yellow needles; it is readily soluble in most organic solvents and when kept for some time parts with its chlorine. On treatment with 2 per cent. sodium hydroxide, or, even better, with warm sodium carbonate, it yields 1-*iodo-3-nitro-5-iodosobenzene* in the form of a pale yellow powder which melts at 118°. Its *acetate*,

$$NO_2 \cdot C_6H_3I \cdot I(OAc)_2,$$

crystallises in colourless plates melting at 172°; its *basic sulphate*, $(C_6H_3O_3NI_2)_2,H_2SO_4$, melts and decomposes at 145° after turning dark coloured at 105°; the *basic nitrate*, $NO_2 \cdot C_6H_3I \cdot I(OH) \cdot NO_3$, is a white, amorphous powder, only sparingly soluble in water, and decomposes at 104°; the *basic chromate*, $[NO_2 \cdot C_6H_3I \cdot I(OH)]_2CrO_4$, is an orange-yellow powder and explodes at 81°; a second *chromate*,



$$NO_2 \cdot C_6H_3I \cdot I{<}\genfrac{}{}{0pt}{}{-O-}{CrO_4}{>}I \cdot C_6H_3I \cdot NO_2,$$

has been obtained by rubbing the iodoso-compound with a solution of chromium trioxide in acetic acid.

Iodonitroiodoxybenzene, $NO_2 \cdot C_6H_3I \cdot IO_2$, obtained by the action of sodium hypochlorite and a little acetic acid on the dichloride, is a pale yellow powder almost insoluble in water or acetic acid and exploding at 187°. Neither a tetrachloride nor a di-iodoxy-compound has been obtained.

s-*Iodonitrophenyl-phenyliodonium hydroxide*, $NO_2 \cdot C_6H_3I \cdot IPh \cdot OH$, has only been obtained in the form of a strongly alkaline, aqueous solution; the *chloride*, $NO_2 \cdot C_6H_3I \cdot IPhCl$, forms long, colourless needles, readily soluble in alcohol or chloroform and melting at 131°. The *bromide* melts at 211° and is insoluble in ether; the *iodide* is an amorphous powder melting at 152° and yields a *periodide*, $NO_2 \cdot C_6H_3I \cdot IPhI_3$, crystallising in red cubes and decomposing at 160°. The *dichromate*, $[NO_2 \cdot C_6H_3I \cdot IPh]_2Cr_2O_7$, forms orange-yellow needles which explode at 160°; the *nitrate* crystallises in yellow needles melting at 138°; the *platinichloride* is a yellowish-red powder which melts and decomposes at 197°, and the *mercurichloride* a flocculent precipitate melting at 198°.

α-Naphthyl-s-*iodonitrophenyliodonium hydroxide*,

$$NO_2\cdot C_6H_3I\cdot I(C_{10}H_7)\cdot OH,$$

obtained by shaking α-iodosonaphthalene and *s*-iodonitroiodoxybenzene with water and silver oxide, gives a strongly alkaline, aqueous solution; the *chloride* forms a white precipitate the *platinichloride* a flesh coloured powder melting at 178° the *bromide* melts at 168°, and the *iodide* melts and decomposes at 89°. The *dichromate* forms a reddish-yellow precipitate and explodes at 154°. *Iodonitrophenyldi-iodonitrophenyliodonium hydroxide*, $OH\cdot I(C_6H_2I_2\cdot NO_2)(C_6H_3I\cdot NO_2)$, obtained as its sulphate by V. Meyer and Hartmann's method, has been converted into the following salts: the *chloride*, a flocculent precipitate, melting at 85°; the *bromide*, a yellow precipitate, melting at 101°; the *iodide*, which begins to decompose at 66° and is completely melted at 98°; the *dichromate*, exploding at 72°; the *platinichloride*, decomposing at 115°; and the *mercurichloride*, melting at 113°.

Dichloroethyl-s-*monoiodonitrophenyliodonium chloride*,

$$ICl(C_2H_3Cl_2)(C_6H_3I\cdot NO_2),$$

obtained from iodonitrophenyliodochloride and acetylene silver–silver chloride melts at 170°; the *bromide* melts at 159°, the *iodide* at 108°, the *nitrate* at 148°, the *dichromate* explodes at 107°, the *platinichloride* melts and decomposes at 162°, and the *mercurichloride* melts at 160°.

J. J. S.

Derivatives of *p*-Iodo*tert.*butylbenzene containing Polyvalent Iodine. By CONRAD WILLGERODT and EBERHARD RAMPACHER (*Ber.*, 1901, **34**, 3666—3678).—*p*-Iodo*tert.*butylbenzene (Pahl, Abstr., 1884, 1009) has been obtained from *p*-*tert.*butylaniline (Louis, *Ber.*, 1883, **16**, 114) by Griess's reaction. It yields a *dichloride*, $C_4H_9\cdot C_6H_4\cdot ICl_2$, crystallising in sulphur-yellow needles, decomposing at 74° and readily soluble in chloroform but insoluble in light petroleum; the dichloride gives an *additive* compound with pyridine which melts at 124°.

p-*Iodoso*tert.*butylbenzene* is a yellow powder decomposing at 189° and sparingly soluble in ether; the *acetate*, $C_4H_9\cdot C_6H_4\cdot I(OAc)_2$, crystallises in large, transparent prisms melting at 95°. p-*Iodoxy*tert.*butylbenzene*, $C_4H_9\cdot C_6H_4\cdot IO_2$, obtained by the action of sodium hypochlorite on the dichloride, is a colourless compound exploding at 201° and is readily soluble in acetic acid.

Di-p-tert.*butylphenyliodonium hydroxide*, $I(C_6H_4\cdot C_4H_9)_2\cdot OH$, has only been obtained in aqueous solution. The *chloride* is a colourless, microcrystalline powder melting at 157° and is only sparingly soluble in hot water. The *bromide* melts at 144°; the *iodide*, obtained by Meyer and Hartmann's method (Abstr., 1894, i, 242), is a yellow, amorphous powder melting and decomposing at 142°; it yields a *periodide*, $I(C_6H_4\cdot C_4H_9)_2\cdot I_3$, crystallising in dark brown needles and melting at 138°. The *nitrate* melts and decomposes at 142° and is only sparingly soluble in water. The *dichromate* decomposes at 105°, the *platinichloride* forms orange coloured plates melting and decomposing at 128—142°, and the *mercurichloride* crystallises in colourless prisms melting at 62°.

Iododi-p-tert.*butylphenyliodonium sulphate* and the *hydroxide*,

$$C_4H_9\cdot C_6H_3I\cdot I(C_6H_4\cdot C_4H_9)\cdot OH,$$

are both readily soluble in water. The *chloride* melts and decomposes at 94°, the *bromide* at 89°, the *iodide* at 86—87°, the *cyanide* readily decomposes, the *dichromate* melts at 118°, the *platinichloride* decomposes at 89°, and the *mercurichloride* melts at 56°. All the salts are comparatively unstable.

Phenyl-p-tert.*butylphenyliodonium chloride*, $C_4H_9{\cdot}C_6H_4{\cdot}IPhCl$, is crystalline and melts at 167°, the *bromide* melts at 157°, the *iodide* at 124°, the *nitrate* crystallises in colourless, glistening needles melting and decomposing at 141° and readily soluble in water or alcohol, the *dichromate* melts at 121°, the *platinichloride* begins to decompose at 152°, and the *mercurichloride* melts at 129°.

Dichloroethyl-p-tert.*butylphenyliodonium chloride*,

$$C_4H_9{\cdot}C_6H_4{\cdot}I(C_2H_3Cl_2)Cl,$$

melts at 107°, the *bromide* crystallises in compact needles melting at 123°, the *iodide* melts at 91°, the *cyanide* rapidly decomposes, the *nitrate* melts at 126°, and the *dichromate* decomposes when removed from its mother liquor. The *picrate* melts at 158°, the *platinichloride* at 64°, and the *mercurichloride* at 73°. J. J. S.

Derivatives of p-*iso*Amylphenyl Iodide containing Polyvalent Iodine.

By CONRAD WILLGERODT and KURT DAMMANN (*Ber.*, 1901, **34**, 3678—3688).—Amino-*p*-*iso*amylbenzene is most readily obtained when aniline, *iso*amyl alcohol, and zinc chloride are heated in molecular proportion at 270—280° (compare Calm, Abstr., 1882, 1284) and is purified by conversion into its sulphate. When diazotised and treated with potassium iodide solution, it yields p-*iodoisoamylbenzene* in the form of a colourless liquid distilling at 281° (corr.). The *dichloride*, $C_5H_{11}{\cdot}C_6H_4{\cdot}ICl_2$, obtained by passing chlorine into a chloroform-acetic acid solution of the iodo-compound kept cool and well stirred, forms crystalline plates melting and decomposing at 84°, and readily soluble in benzene, ether, or chloroform; when kept, it gives up part of its chlorine. The *iodoso*-compound forms a snow-white powder melting and decomposing at 162° and is insoluble in water. The *acetate*, $C_5H_{11}{\cdot}C_6H_4{\cdot}I(OAc)_2$, crystallises in long, colourless needles melting and decomposing at 78°. p-*Iodoxy*isoamyl*benzene*, $C_5H_{11}{\cdot}C_6H_4{\cdot}IO_2$, after extraction with ether and 10 per cent. acetic acid, crystallises from hot water in glistening plates which explode at 200—203°.

Di-p-iso*amylphenyliodonium chloride*, $I(C_6H_4{\cdot}C_5H_{11})_2Cl$, crystallises in needles melting at 74°; the *platinichloride* melts and decomposes at 178°, and the *mercurichloride* crystallises in plates decomposing at 163°. The *bromide* melts at 127°; the *iodide* melts at 68° and is converted into *p*-iodoamyl benzene. The *dichromate* decomposes at 137°.

Phenyl-p-iso*amylphenyliodonium chloride*, $C_5H_{11}{\cdot}C_6H_4{\cdot}IPhCl$, crystallises in needles decomposing at 159°; the *platinichloride* is an orange coloured powder melting and decomposing at 165°, and the *mercurichloride* crystallises in glistening needles melting and decomposing at 132°. The *bromide* melts at 145°, the *iodide* melts at 118° and is at the same time decomposed into phenyl iodide and *p*-iodoamylbenzene; the *trichloroacetate* melts and decomposes at 85°, and the *nitrate* melts at 122°.

p-iso*Amylphenyl-a-naphthyliodonium chloride*, $C_5H_{11}{\cdot}C_6H_4{\cdot}I(C_{10}H_7)Cl$, melts at 152°; the *platinichloride* melts and decomposes at 162°, and the *mercurichloride* at 141°. The *bromide* melts at 156°, the *iodide* melts and decomposes at 134°, and the *dichromate* melts at 74° and explodes at 90°.

p-iso*Amylphenyldichloroethyliodonium chloride* melts at 132°, the *bromide* melts and decomposes at 109°, and the *iodide* at about 60°. The *nitrate* crystallises in long, glistening needles and melts at 82°; the *sulphate* melts and decomposes at 56°, and the *platinichloride* forms reddish-yellow crystals melting and decomposing at 124°.

J. J. S.

Phenylated Naphthenes. Phenyl*cyclo*hexane and its Derivatives. By NICOLAI KURSANOFF (*Annalen*, 1901, **318**, 309—326. Compare Willstätter and Lessing, Abstr., 1901, i, 265).—*Phenyl*cyclo*hexane*, $C_6H_{11}Ph$, prepared by adding *cyclo*hexyl chloride to a cooled mixture of benzene and anhydrous aluminium chloride, melts at 7°, boils at 239° under 745 mm. pressure, and has a sp. gr. 0·9441 at 20°/0°. The yield of this hydrocarbon decreases as the quantity of aluminium chloride employed increases. A higher fraction boiling at 200—315° under 20—22 mm. pressure is also obtained in the preceding condensation; it yields a small quantity of a solid hydrocarbon, o-*diphenyl*cyclo*hexane*, crystallising from alcohol in needles and melting at 170—171°; the residual oil, when oxidised with dilute nitric acid, yields *iso*phthalic acid, this result indicating that the liquid probably contains m-*diphenyl*cyclo*hexane*. The relative position of the phenyl radicles in *o*-diphenyl*cyclo*hexane is determined by preparing the hydrocarbon from pure o-dichloro*cyclo*hexane.

Barium cyclo*hexylbenzenesulphonate*, $(C_6H_{11}\cdot C_6H_4\cdot SO_3)_2Ba$, produced by dissolving phenyl*cyclo*hexane in cold, fuming sulphuric acid, and converting the product into the barium salt, separates in anhydrous flakes which are sparingly soluble in cold water. The *sodium* and *potassium* salts are obtained in ill-defined crystals on adding the sulphonation product to concentrated solutions of the corresponding chlorides. The *sulphonic acid*, isolated by decomposing the *lead* salt with hydrogen sulphide, crystallises from mixtures of chloroform and benzene, or light petroleum, in slender needles and decomposes at 114—116°; it is probably a para-derivative.

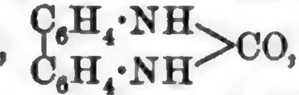
p-*Nitro*cyclo*hexylbenzene*, $C_6H_{11}\cdot C_6H_4\cdot NO_2$, produced by adding phenyl*cyclo*hexane to fuming nitric acid (4—5 parts), crystallises from alcohol in well-defined prisms and melts at 57·5—58·5°; it is oxidised to *p*-nitrobenzoic acid when heated with dilute nitric acid for 60 hours.

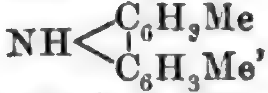
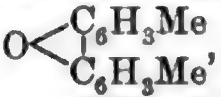
p-*Amino*cyclo*hexylbenzene*, $C_6H_{11}\cdot C_6H_4\cdot NH_2$, obtained on reducing the corresponding nitro-compound with tin and hydrochloric acid, crystallises from light petroleum in leaflets melting at 54—56°; it is volatile in steam. The *sulphate*, $(C_{12}H_{15}\cdot NH_2)_2,H_2SO_4$, crystallises in silky needles and decomposes at 287—290°. The *hydrochloride*, *hydrobromide*, and *nitrate* crystallise in leaflets and decompose at 261—262°, 280—282°, and 225—227° respectively. The *acetyl* derivative, $C_{12}H_{15}\cdot NHAc$, and the *thiocarbamide* melt at 128—129·5° and 157—158° respectively.

p-cyclo*Hexylbenzenediazonium sulphate*, $(C_6H_{11}\cdot C_6H_4\cdot N_2)_2SO_4$, results from the action of sodium nitrite on *p*-amino*cyclo*hexylbenzene sulphate suspended in dilute sulphuric acid; it is only moderately soluble in water, and when treated with an alkaline solution of β-naphthol yields the red *azo*-compound, $C_6H_{11}\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$.

p-cyclo*Hexylphenol*, $C_6H_{11}\cdot C_6H_4\cdot OH$, produced by heating a solution of the diazonium salt on the water-bath, crystallises from benzene or light petroleum in needles melting at 132—133°. This phenol is volatile in steam and only slightly soluble in water; its *sodium* and *potassium* derivatives dissolve but sparingly in water and are insoluble in solutions of the alkali hydroxides; the latter compound, $C_6H_{11}\cdot C_6H_4\cdot OK$, crystallises in long needles.

Phenyl*cyclo*hexane reacts with bromine evolving hydrogen bromide, and when oxidised with nitric acid or potassium permanganate or dichromate yields benzoic acid. G. T. M.

Derivatives of Diphenyl. By STEFAN VON NIEMENTOWSKI (*Ber.*, 1901, **34**, 3325—3337).—Details are given of a method by which a 60 per cent. yield of 2 : 2′-dinitrodiphenyl may be obtained from *o*-nitroaniline, by the action of copper on the diazo-compound (compare Ullmann and Bielecki, Abstr., 1901, i, 586); this substance is identical with the compound prepared by Täuber (Abstr., 1891, 570) from dinitrobenzidine and is reduced by tin and hydrochloric acid to 2 : 2′-diaminodiphenyl. 2 : 2′-*Diformylaminodiphenyl*, $C_{12}H_8(NH\cdot CHO)_2$, crystallises from alcohol in stout crystals and melts at 137°. The *dibenzoyl* derivative, $C_{12}H_8(NHBz)_2$, crystallises from alcohol in stout crystals, softens at 176°, and melts at 184°. *Carbonyl*-2 : 2′-*diaminodiphenyl*,  $\begin{matrix}C_6H_4\cdot NH\\ |\\ C_6H_4\cdot NH\end{matrix}>CO$, separates from glacial acetic acid in glistening crystals and melts at 310°.

2 : 2′-*Diamino*-4 : 4′-*dimethyldiphenyl*, $C_{12}H_6Me_2(NH_2)_2$, crystallises from alcohol in needles and melts at 120°. The *diformyl* derivative crystallises from alcohol in stout crystals or needles, softens at 185° and melts at 187°. The *diacetyl* derivative crystallises from alcohol in stout crystals or in needles and melts at 189°. The *dibenzoyl* derivative crystallises from alcohol in needles and melts at 170°. *Carbonyl*-2 : 2′-*diamino*-4 : 4′-*dimethyldiphenyl* crystallises from acetic acid in snow-white, woolly needles containing ½ mol. $C_2H_4O_2$ and melts at 339°. The *dibenzylidene* derivative crystallises from acetic acid in yellow needles and melts at 242°. 2 : 7-*Dimethylcarbazole*,  $NH<\begin{matrix}C_6H_3Me\\ |\\ C_6H_3Me\end{matrix}$, prepared from diaminodimethyldiphenyl by Täuber's method (Abstr., 1893, i, 588), crystallises from alcohol and melts at 283°. 4 : 4′-*Dimethyldiphenyleneoxide*,  $O<\begin{matrix}C_6H_3Me\\ |\\ C_6H_3Me\end{matrix}$, prepared by the method of Täuber and Halberstadt (Abstr., 1892, 1470), crystallises from alcohol in glistening flakes and melts at 82°. T. M. L.

Action of Nitrogen Trioxide and Peroxide on Stilbene. II. By JULIUS SCHMIDT (*Ber.*, 1901, **34**, 3536—3543. Compare Abstr., 1901, i, 266).—Gabriel's 'stilbene dinitrite' (Abstr., 1885, 1229) is identical with the *s*-α-diphenyldinitroethane described by the author (*loc. cit.*); the melting point given by Gabriel is incorrect. *s*-β-*Diphenyldinitroethane*, formed along with stilbene nitrosite by the action of nitrous fumes on stilbene, crystallises from acetic acid in stout, white prisms, melts at 150—152° to a yellow liquid, and decomposes at 200°; the α- and β-compounds are related to one another in the same way as mesotartaric and racemic acids, and both yield the same tetraphenylpiperazine. T. M. L.

Interaction of Aliphatic Disulphonic Chlorides and Aromatic Amino-compounds. By WILHELM AUTENRIETH and P. RUDOLPH (*Ber.*, 1901, **34**, 3467—3482).—Ethylenedisulphonic chloride interacts with aniline (3 mols.) in benzene solution with elimination of sulphur dioxide (1 mol.) and hydrogen chloride (1 mol.) to form *vinylsulphanilide*, $CH_2{:}CH\cdot SO_2\cdot NHPh$, which crystallises in lustrous leaflets, melts at 68°, and, although an unsaturated compound, is not reduced by sodium amalgam, and does not combine with bromine. On hydrolysis with hydrochloric acid, it yields aniline and *iso*ethionic acid, the latter being formed by the addition of $1H_2O$ to the vinylsulphonic acid which is first produced. *Vinylsulphonmethylanilide*,

$$CH_2{:}CH\cdot SO_2\cdot NMePh,$$

obtained either by the interaction of ethylenedisulphonic chloride and methylaniline or by methylating vinylsulphanilide, crystallises from dilute alcohol, melts at 79°, and is hydrolysed by boiling with hydrochloric acid to methylaniline and *iso*ethionic acid. *Vinylsulphonbenzanilide*, $CH_2{:}CH\cdot SO_2\cdot NPh\cdot C_7H_7$, crystallises from dilute alcohol in slender prisms melting at 87°; *vinylsulphonacetanilide*,

$$CH_2{:}CH\cdot SO_2\cdot NPhAc,$$

separates from the same solvent in slender needles and melts at 100°.

Propylenesulphanilide, $CHMe{:}CH\cdot SO_2\cdot NHPh$, prepared from propylenedisulphonic chloride, crystallises from alcohol in needles or leaflets and melts at 91°; the corresponding methylanilide is similar and melts at 58°.

Trimethylenedisulphonanilide, $CH_2(CH_2\cdot SO_2\cdot NHPh)_2$, obtained by warming trimethylenedisulphonic chloride with aniline dissolved in benzene, crystallises from alcohol in lustrous leaflets and melts at 130°; it is not hydrolysed by hot dilute acids or alkalis and yields an amorphous *silver* salt, $C_{15}H_{16}O_4N_2S_2Ag_2$, which is decomposed by warm water.

Trimethylenedisulphonbenzanilide, $CH_2(CH_2\cdot SO_2\cdot NPh\cdot C_7H_7)_2$, forms slender, colourless needles melting at 160°; *trimethylenedisulphonacetanilide* is similar and melts at 176°.

Ethylsulphanilide, $C_2H_5\cdot SO_2\cdot NHPh$, obtained from ethylsulphonic chloride and aniline, forms colourless needles and melts at 55°; the *benzylanilide* crystallises in lustrous leaflets and melts at 100°, and the *acetylanilide* in rhombic plates melting at 110°.

All the foregoing anilides have a strongly acid character, being soluble in dilute aqueous alkalis. It should be noted that in their formation sulphur dioxide is eliminated only in the case of the αβ- and not in that of αγ-disulphonic chlorides; the former yield monosulphanilides, the latter disulphanilides. W. A. D.

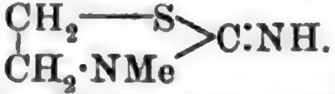
Compounds of the Ethylenimine Series. By WILHELM MARCKWALD and O. FROBENIUS (*Ber.*, 1901, **34**, 3544—3558).—p-*Toluenesulphonmethylbromoethylamide*, $C_6H_4Me\cdot SO_2\cdot NMe\cdot CH_2\cdot CH_2Br$, prepared by heating dry sodium toluenesulphonmethylamide with ethylene bromide, separates from carbon disulphide in white crystals, melts at

76·5°, and is readily soluble in most solvents; when heated with strong hydrobromic acid at 160°, it is decomposed into toluene, sulphuric acid, and methylbromoethylamine.

Methylbromoethylamine, $NHMe\cdot CH_2\cdot CH_2Br$, yields a *platinichloride* which forms dark red crystals, dissolves readily in water, and melts at 202—203°; the *picrate* forms orange crystals, dissolves in hot water, and melts at 114°.

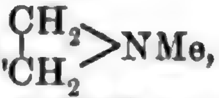
p-*Toluenesulphon-β-naphthoxymethylethylamide*,

$$C_6H_4Me\cdot SO_2\cdot NMe\cdot CH_2\cdot CH_2\cdot O\cdot C_{10}H_7,$$

forms white crystals, dissolves readily in boiling alcohol and melts at 109·5°. *Methylchloroethylamine*, $NHMe\cdot CH_2\cdot CH_2Cl$, prepared by heating the preceding compound with hydrochloric acid at 170°, yields a *hydrochloride* which crystallises from hot acetone in white, hygroscopic crystals and melts at 108—112°; the *platinichloride* crystallises from hot alcohol and melts at 219°; the *picrate* forms yellow crystals and melts at 105°; when heated with water and a little hydrogen chloride, the base gives Knorr and Matthes' methylethanolamine, $NHMe\cdot CH_2\cdot CH_2\cdot OH$ (Abstr., 1898, i, 399); with sodium sulphocyanide, it gives methyliminothiazolidine,  $\begin{matrix}CH_2\text{——}S\\ | \\ CH_2\cdot NMe\end{matrix}\!>\!C{:}NH$.

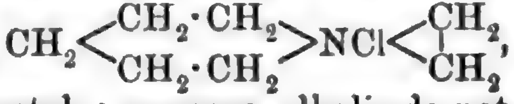
Methylchloroethylbenzamide, $NMeBz\cdot CH_2\cdot CH_2Cl$, when boiled with water, is converted into *benzoylethanolmethylamine*, $NHMe\cdot CH_2\cdot CH_2\cdot OBz$, an oily base, the *hydrochloride* of which crystallises from acetone in white, glistening flakes, dissolves readily in water, and melts at 143°; the corresponding *platinichloride* forms a golden-yellow powder and melts at 195°; the *picrate* forms yellow crystals and melts at 155°; the constitution of this base was proved by hydrolysis to benzoic acid and methylethanolamine.

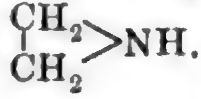
Benzoylethanolnitrosomethylamine, $NO\cdot NMe\cdot CH_2\cdot CH_2\cdot OBz$, is a yellow oil.

N-*Methylethylenimine*,  $\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}\!>\!NMe$, prepared by the action of alkalis on chloroethylamine, boils at 27·5° under 764 mm. pressure; it is a mobile liquid which fumes in the air, is miscible with water, has a sp. gr. 0·7572 at 19·5°, coefficient of refraction 0·3885 at 19°, $M_D = 17·78$; the *picrate* forms yellow crystals and melts at 120—122°; the *aurichloride* is a yellow, crystalline precipitate and melts at 95°; the base is stable towards permanganate and bromine water, but is converted by hydrochloric acid to chloroethylmethylamine, by sulphur dioxide to methyltaurine, by dilute sulphuric acid to methylethanolamine, and by methyl iodide to trimethyliodoethylammonium iodide, $CH_2I\cdot CH_2\cdot NMe_3I$, but is indifferent towards carbon disulphide and ethyl oxalate.

Benzenesulphonmethylchloroethylamide, $C_6H_5\cdot SO_2\cdot NMe\cdot CH_2\cdot CH_2Cl$, prepared by the action of benzoyl chloride on the base, crystallises from light petroleum in white needles melting at 65—66°; similarly with benzoyl chloride, it yields methylchloroethylbenzamide.

A *polymeric* base, $C_6H_{14}N_2$, is also formed by the action of alkalis on methylchloroethylamine; it boils at 128—130° and is dibasic; the *picrate*, $C_6H_{14}N_2(C_6H_3O_7N_3)_2$, forms a yellow, crystalline precipitate and decomposes at 260° without melting; the *platinichloride* is an orange coloured, crystalline precipitate and melts and decomposes at 163°; the base is stable towards acids, reduces alkaline permanganate, is not identical with N-dimethylpiperazine, yields a soluble *ferrocyanide* which forms a white, soluble powder, and is therefore probably a tertiary base.

1-β-*Naphthoxyethylpiperidine*, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot OC_{10}H_7$, crystallises from light petroleum in white needles and melts at 47—49°; the *hydrochloride* forms white crystals, and the *platinichloride* large crystals, which soften at 90°, and melt and decompose at 100—110°; the *picrate* crystallises from alcohol and melts at 160—161°; the *dichromate* is insoluble in water or alcohol. 1-*Chloroethylpiperidine*, $C_5NH_{10}\cdot CH_2\cdot CH_2Cl$, prepared by heating the preceding base with hydrochloric acid at 150°, is a yellow oil, moderately soluble in water; the *hydrochloride* separates from acetone in white crystals and becomes brown and melts at 208°; the yellow *aurichloride* is readily soluble in hot water and in alcohol and melts at 119—120°; the *picrate* crystallises from alcohol and melts at 116—117°. When heated with dilute sulphuric acid, the base is converted into Ladenburg's 1-β-hydroxyethylpiperidine (Abstr., 1882, 165). When heated, the chloroethylpiperidine is converted by isomeric change into *ethylenepiperidinium chloride*,  $\mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix}{>}\mathrm{NCl}{<}\begin{smallmatrix}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{smallmatrix}$, which separates from alcohol in white crystals; aqueous alkalis do not precipitate a base, but when the chloride is acted on by silver oxide, an alkaline solution is obtained which leaves a syrupy, quaternary base on evaporation; the *platinichloride* is an orange-coloured, insoluble precipitate; the *aurichloride* forms yellow, insoluble crystals and melts and decomposes at 273—274°; when heated on a water-bath with concentrated hydrochloric acid for an hour, the base is reconverted into chloroethylpiperidine hydrochloride.

The study of the two polymethylenimine bases here described has completely confirmed Howard and Marckwald's view (Abstr., 1900, i, 749) that Gabriel's 'vinylamine' is a ring-compound, as represented by the formula  $\begin{smallmatrix}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{smallmatrix}{>}\mathrm{NH}$. T. M. L.

Bromoallylamine. By H. Rudzick (*Ber.*, 1901, **34**, 3543).—In order to ascertain whether the two bases described by Paal (Abstr., 1889, 117) were ethylene or polymethylenimine derivatives, bromoallylamine was treated with toluenesulphonic chloride. *Toluene* p-*sulphobromoallylamide*, $C_6H_4Me\cdot SO_2\cdot NH\cdot C_3H_4Br$, crystallises from light petroleum and melts at 45—46°; it dissolves completely in alkalis, showing that the base is a primary amine, as suggested by Paal, and not a ring-compound. T. M. L.

Action of Ammonia on Benzyl Chloride, and the Conditions of Formation of Benzylamine. By René Dhommée (*Compt. rend.*, 1901, **133**, 636—638. Compare Mason, Trans., 1893, **63**, 1313).—The author has investigated the conditions under which benzyl chloride and ammonia give the best yield of benzylamine. The reaction takes place most rapidly in the presence of ethyl alcohol, and is retarded by the use of higher alcohols (amyl) as solvent. When a large excess of a saturated solution of ammonia in 60 per cent. alcohol at a temperature of 15° was employed, 44·5 per cent. of the benzyl chloride was converted into benzylamine, only a small quantity of dibenzylamine and no tribenzylamine being formed at the same time.

K. J. P. O.

m-Cyanobenzyl Chloride. By Felix Ehrlich (*Ber.*, 1901, **34**, 3366—3377).—*m*-Cyanobenzylphthalimide is converted by alcoholic potash into m-*cyanobenzylphthalamic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CN,$$

which crystallises in small, silky needles and melts at 175°, losing water and reforming the phthalimide. When the aqueous solution of the acid is evaporated, a portion of the substance is reconverted into the phthalimide, whilst the remainder is hydrolysed with formation of cyanobenzylamine and phthalic acid. m-*Cyanobenzylamine*,

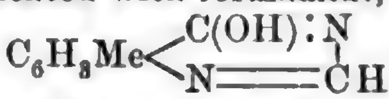
$$CN\cdot C_6H_4\cdot CH_2\cdot NH_2,$$

is a brownish coloured oil, which is miscible with water and unites with the carbon dioxide of the atmosphere. The *hydrochloride* melts at 221—222°; the *picrate*, $C_8H_8N_2,C_6H_3O_7N_3,\frac{1}{2}H_2O$, melts and decomposes at 217°; the *platinichloride* melts at 240° and the *oxalate* melts and decomposes at 196·5°. *Di*-m-*cyanobenzylamine*, $NH(CH_2\cdot C_6H_4\cdot CN)_2$, is formed by the action of alcoholic ammonia on cyanobenzyl chloride and crystallises in matted needles which are sparingly soluble in water and melt at 54°. The *hydrochloride* melts at 234—235°; the *platinichloride* melts and decomposes at 231°; the *aurichloride* melts at 209°, the *picrate* melts at 170°, and the *dichromate* decomposes at above 250°. *Tri*-m-*cyanobenzylamine*, $N(CH_2\cdot C_6H_4\cdot CN)_3$, is formed together with the foregoing compound and by the action of cyanobenzyl chloride on dicyanobenzylamine, and crystallises in rhombic tablets melting at 118—119°. The *hydrochloride* is decomposed by water. The base is converted by hydrochloric acid at 120—130° into *tribenzylamine*-m-*tricarboxylic acid*, $N(CH_2\cdot C_6H_4\cdot CO_2H)_3$, which crystallises in microscopic needles and melts and decomposes at 248—249°. m-*Cyanobenzyl thiocyanate* is obtained by the action of the chloride on potassium thiocyanate and crystallises in plates, tablets, or small prisms melting at 55°. On hydrolysis with hydrochloric acid at the atmospheric pressure, it yields m-*dicarboxybenzyl sulphide*,

$$S(CH_2\cdot C_6H_4\cdot CO_2H)_2,$$

crystallising in fascicular groups of silky needles which melt at 197°; the *silver* salt is a white precipitate. Hydrochloric acid at 170° converts the thiocyanate into m-*dicarboxybenzyl disulphide*,

$$S_2(CH_2\cdot C_6H_4\cdot CO_2H)_2,$$

which crystallises in needles melting at 200—202° and can also be prepared from *m*-cyanobenzyl disulphide by hydrolysis. The thiocyanate is converted by the action of hydrogen sulphide into m-*cyanobenzyl disulphide*, $S_2(C_7H_6\cdot CN)_2$, which forms radiating groups of needles and melts at 116—117°. m-*Cyanobenzyl sulphide*, $S(C_7H_6\cdot CN)_2$, obtained by the action of potassium sulphide on cyanobenzyl chloride, crystallises in stellate and fan-shaped groups of prisms, melting at 99·5°. Nitric acid converts it almost quantitatively into *iso*phthalic acid. m-*Cyanobenzyl mercaptan*, $CN\cdot C_6H_4\cdot CH_2\cdot SH$, is prepared by the action of the chloride on potassium hydrogen sulphide, and crystallises in spherical masses melting at 24—25°; oxidation converts it into the disulphide. p-*Nitro*-m-*cyanobenzyl chloride*, $CN\cdot C_6H_3(NO_2)\cdot CH_2Cl$, is obtained by the action of nitric acid on the chloride and crystallises in brownish-yellow plates melting at 59—60°. The *anilide* melts at 135°. On reduction, it is converted into p-*amino*-m-*toluonitrile*, $CN\cdot C_6H_3Me\cdot NH_2$ [$Me:CN:NH_2 = 1:3:4$], which crystallises in lustrous needles or plates melting at 60—61°, and is converted by hydrochloric acid at 100° into 4-amino-*m*-toluic acid melting at 172·5°. The hydrochloride of this amino-acid melts at 200—201°, whilst it is stated by Panaotovic (*J. pr. Chem.*, 1886, [ii], **33**, 62) to melt at 207°. When heated with formamide, the acid yields 4-*hydroxy*-6-*methylquinazoline*,  $C_6H_3Me<\begin{matrix} C(OH):N \\ N\text{===}CH \end{matrix}$, melting at 251° and forming a *platinichloride* which melts and decomposes at about 290°. This reaction proves that the aminotoluic acid actually has the constitution assigned to it above. p-*Cyanobenzylphthalamic acid* crystallises in nacreous plates and melts and decomposes at 192°. p-*Cyanobenzylamine* is a basic oil; the *hydrochloride* melts at 274°; the *picrate* melts at 218°, and the *platinichloride* melts and decomposes at 250°. A. H.

Some Acetyl- and Benzoyl-ψ-thiocarbamides. By HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1901, **26**, 408—418).—The acyliminodithiocarbonic esters (Abstr., 1901, i, 705) react with amines at the ordinary temperature with formation of acyl-ψ-thiocarbamides, thus: $NBz\dot{:}C(SMe)_2 + NHRR' = NBz\dot{:}C(SMe)\cdot NRR' + MeHS$. The acyl-ψ-thiocarbamides have no basic properties; those which contain a NH group are soluble in alkali; those derived from primary amines are decomposed by heat with formation of mercaptan, substituted acid amides, and other products, whilst those derived from secondary amines can be distilled under reduced pressure without decomposition. When treated with hydrochloric acid, they undergo hydrolysis in the following manner: $NBz\dot{:}C(SEt)\cdot NHPh + H_2O = NHBz\cdot CO\cdot SEt + C_6H_5\cdot NH_2$. By the action of alcoholic ammonia, guanidine derivatives are formed. They readily react with phenylhydrazine with production of aminotriazoles.

When dimethyl acetyliminodithiocarbonate is treated with alcoholic ammonia, guanidine is produced. *Acetyldi*iso*butylthiolmethyl-ψ-thiocarbamide*, $NAc\dot{:}C(SMe)\cdot N(C_4H_9)_2$, is a yellow oil which boils at 175—177° under 22 mm. pressure. *Acetylphenylthiolmethyl-ψ-thiocarbamide*, $NAc\dot{:}C(SMe)\cdot NHPh$, forms long, colourless needles and melts at 82—83°. *Benzoyl*-p-*tolylthiolmethyl-ψ-thiocarbamide*,

$$NBz\dot{:}C(SMe)\cdot NH\cdot C_6H_4Me,$$

crystallises in prisms and melts at 130°. *Benzoyl-a-naphthylthiolmethyl-ψ-thiocarbamide*, $NBz\dot{:}C(SMe)\cdot NH\cdot C_{10}H_7$, crystallises in slender needles and melts at 124°. *Benzoyl*-m-*nitrophenylthiolmethyl-ψ-thiocarbamide*, $NBz\dot{:}C(SMe)\cdot NH\cdot C_6H_4\cdot NO_2$, crystallises in prisms and melts at 71—72°. *Acetyldiethylthiolethyl-ψ-thiocarbamide*, $NAc\dot{:}C(SEt)\cdot NEt_2$, is a yellow oil which distils at 162—164° under 21 mm. pressure. *Acetylphenylmethylthiolethyl-ψ-thiocarbamide*, $NBz\dot{:}C(SEt)\cdot NMePh$, crys-

tallises in prisms and melts at 66°. *Benzoyldiethylthiolethyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SEt)\cdot NEt_2}$, forms colourless, rectangular prisms and melts at 70°. *Benzoyldipropylthiolethyl-ψ-thiocarbamide*,
$\mathrm{NBz{:}C(SEt)\cdot NPr_2}$,
is a yellow oil which boils at 226—229° under 17 mm. pressure. *Benzoyldiisobutylthiolethyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SEt)\cdot N(C_4H_9)_2}$, boils at 234—236° under 21 mm. pressure. *Benzoyl-*p*-tolylthiolethyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SEt)\cdot NH\cdot C_6H_4Me}$, crystallises in prisms and melts at 93°; it reacts with phenylhydrazine with formation of mercaptan and *diphenyl-*p*-tolylaminotriazole*, which crystallises in stout prisms and melts at 225—226°. *Benzoyl-ψ-cumylthiolethyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SEt)\cdot NH\cdot C_6H_2Me_3}$, forms slender needles and melts at 83—84°. *Benzoyl-*p*-anisylthiolethyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SEt)\cdot NH\cdot C_6H_4\cdot OMe}$, crystallises in slender prisms and melts at 99—100°. *Benzoyldiphenylthiolethyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SEt)\cdot NPh_2}$, crystallises in prisms and melts at 142°. *Benzoylphenylthiolpropyl-ψ-thiocarbamide*,
$\mathrm{NBz{:}C(SPr)\cdot NHPh}$,
crystallises in prisms and melts at 78—79°. *Benzoyl-*p*-tolylthiolpropyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SPr)\cdot NH\cdot C_6H_4Me}$, crystallises in needles and melts at 81—81·5°. *Benzoyl-*m*-chlorophenylthiolpropyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(SPr)\cdot NH\cdot C_6H_4Cl}$, forms colourless prisms and melts at 59—59·5°. *Benzoylphenyleneguanidine*, $\mathrm{NBz{:}C{:}(NH)_2{:}C_6H_4}$, obtained by the action of *o*-phenylenediamine on diethylbenzoyliminodithiocarbonate, crystallises in minute prisms and melts at 237°. *Diphenylenebisbenzoylthiolethyl-ψ-thiocarbamide*, $\mathrm{C_{12}H_8[NH\cdot C(SEt){:}NBz]_2}$, crystallises in needles and melts and decomposes at 179°; it reacts with phenylhydrazine to form the *bistriazole*, $\mathrm{C_{12}H_8(NH\cdot C_2N_3Ph_2)_2}$, which crystallises from alcohol and does not melt below 265°. *Dimethoxydiphenylenebisbenzoylthiolethyl-ψ-thiocarbamide*,
$\mathrm{C_{12}H_6(OMe)_2[NH\cdot C(SEt){:}NBz]_2}$,
crystallises in minute, colourless needles and melts at 170—171°. *Benzoylphenylthiolbenzyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(S\cdot C_7H_7)\cdot NHPh}$, may be prepared by the action of aniline on benzyl benzoyliminodithiocarbonate, by the action of benzoic anhydride on phenylbenzyl-ψ-thiocarbamide, or by the action of benzyl chloride on benzoylphenylthiocarbamide in presence of sodium hydroxide or sodium ethoxide; it crystallises in small prisms and melts at 116—117°. When this compound is warmed with hydrochloric acid, *thiobenzylbenzoylcarbamate*, $\mathrm{NHBz\cdot CO\cdot S\cdot C_7H_7}$, is produced, which crystallises in needles and melts at 141—142°. *Benzoylphenylguanidine*, $\mathrm{NBz{:}C(NH_2)\cdot NHPh}$, obtained by the action of alcoholic ammonia on benzoylphenylthiolbenzyl- or benzoylphenylthiolethyl-ψ-thiocarbamide, crystallises in minute, light yellow prisms and melts at 90—91°; the *picrate* melts at 186°. *Benzoylphenylthiol-*m*-xylyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C(S\cdot C_8H_9)\cdot NHPh}$, crystallises in prisms and melts at 110—111°. *Benzoyl-α-naphthylthiol-*m*-xylyl-ψ-thiocarbamide*, $\mathrm{NBz{:}C\cdot(SC_8H_9)\cdot NH\cdot C_{10}H_7}$, forms colourless, flattened prisms and melts at 133°.

E. G.

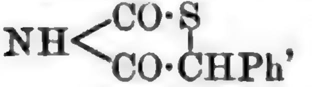
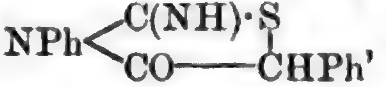
Action of Benzoyl Chloride on Ammonium Thiocyanate. By Gideon Benson and Homer W. Hillyer (*Amer. Chem. J.*, 1901, **26**, 373—377).—When ammonium thiocyanate (1 mol.) is heated with benzoyl chloride (3 mols.), hydrogen chloride, carbon dioxide, and carbon oxysulphide are evolved, and benzoic acid and benzonitrile are produced. Estimation of the products shows that the reaction proceeds in accordance with the following equation:

$$3C_6H_5\cdot COCl + NH_4CNS = 2C_6H_5\cdot CN + C_6H_5\cdot CO_2H + 3HCl + COS.$$

E. G.

Thiocyanates and *iso*Thiocyanates. [Thiocarbimides]. By HENRY L. WHEELER [and, in part, TREAT B. JOHNSON] (*Amer. Chem. J.*, 1901, **26**, 345—360).—*Diethyl thiocyanomalonate*, $NCS\cdot CH(CO_2Et)_2$, obtained by warming diethyl chloromalonate with potassium thiocyanate, is a colourless oil which boils at 169—170° under 22—23 mm. pressure; by the action of strong hydrochloric acid, it is converted into 3 : 5-diketotetrahydrothiazole. When diethyl thiocyanomalonate is heated with thiobenzoic acid, the *diethyl malonate* derivative of *benzoyldithiocarbamic acid*, $NHBz\cdot CS_2\cdot CH(CO_2Et)_2$, is produced, which forms long, yellow, flattened prisms or plates and melts at 119°.

When tricarbethoxychloromethane is boiled with alcoholic potassium thiocyanate, no reaction takes place.

Ethyl phenylchloroacetate boils at 142—145° under 17—18 mm. pressure, and when warmed with alcoholic ammonium thiocyanate yields *ethyl phenylthiocyanoacetate*, $NCS\cdot CHPh\cdot CO_2Et$, which boils at 182—184° under 17 mm. pressure; this substance is converted by concentrated hydrochloric acid into 2-*phenyl*-3 : 5-*diketotetrahydrothiazole*,  $NH{<}\begin{array}{l}CO\cdot S\\ CO\cdot CHPh\end{array}$, which crystallises in colourless prisms, melts at 125—126°, and dissolves readily in alcohol and sparingly in water. By the action of aniline on ethyl phenylthiocyanoacetate, *diphenyl-ψ-thiohydantoin*,  $NPh{<}\begin{array}{l}C(NH)\cdot S\\ CO\text{——}CHPh\end{array}$, is obtained, which crystallises in needles or plates and melts at 185—186°. When ethyl phenylthiocyanoacetate is heated with thiobenzoic acid, the *ethyl phenylacetate* derivative of *benzoyldithiocarbamic acid*, $NHBz\cdot CS_2\cdot CHPh\cdot CO_2Et$, is produced, which crystallises in thin, yellow plates and melts at 150—154°.

Diphenylmethylthiocarbimide, $CHPh_2\cdot NCS$, obtained by heating diphenylmethyl bromide with ammonium or potassium thiocyanate, distils at 222—225° under 37—38 mm. pressure as a blue liquid which solidifies on cooling; it crystallises from alcohol in colourless prisms and melts at 61°. *Diphenylmethylacetamide*, $CH_3\cdot CO\cdot NH\cdot CHPh_2$, formed by the action of thioacetic acid on the thiocarbimide, crystallises in colourless needles, melts at 146—147°, and is readily hydrolysed by strong hydrochloric acid with production of benzhydrylamine hydrochloride. The corresponding *benzamide*, $C_6H_5\cdot CO\cdot NH\cdot CHPh_2$, crystallises in silky needles and melts at 166—167°. *Diphenylmethylthiocarbamide*, $CHPh_2\cdot NH\cdot CS\cdot NH_2$, obtained by the action of ammonia on the thiocarbimide, forms long, silky needles and melts at 189°. *Diphenylmethylmethylthiocarbamide*, $CHPh_2\cdot NH\cdot CS\cdot NHMe$, crystallises in colourless, flattened prisms and melts at 152°. *Diphenylmethyldiethylthiocarbamide*, $CHPh_2\cdot NH\cdot CS\cdot NEt_2$, crystallises in colourless needles and melts at 112—113°; *diphenylmethyldi*iso*butylthiocarbamide* forms long, colourless needles and melts at 97—98°. Diphenylmethylphenylthiocarbamide melts at 178°. *Diphenylmethylphenylmethylthiocarbamide*, $CHPh_2·NH·CS·NPhMe$, crystallises in long, slender needles and melts at 119—120°; *diphenylmethyl-β-naphthylthiocarbamide*, $CHPh_2·NH·CS·NH·C_{10}H_7$, forms colourless needles and melts at 179°. *Diphenylmethylphenylthiosemicarbazide*,

$$CHPh_2·NH·CS·NPh·NH_2,$$

crystallises in colourless plates and melts at 178°; if the temperature is maintained at 178°, or a little higher, for a few seconds, the substance solidifies, and then melts and decomposes at 198°.

When triphenylmethyl thiocyanate is heated with thioacetic acid, *triphenylmethyl thiolacetate*, $CH_3·CO·S·CPh_3$, is obtained, which crystallises in colourless prisms and melts at 138—140°. The corresponding *thiolbenzoate* forms colourless prisms and melts at 184—185°. If a solution of triphenylmethyl thiocyanate in benzene is mixed with alcoholic ammonia, left for three days, and then evaporated to dryness, a residue is obtained, part of which is soluble in water and the remainder in benzene; the aqueous solution contains triphenylmethylcarbinol and ammonium thiocyanate, whilst the benzene solution, after treatment with dry hydrogen chloride, yields triphenylmethylamine hydrochloride and triphenylmethyl ethyl ether. By the action of aniline on triphenylmethyl thiocyanate, phenylthiocarbamide is produced. Phenylhydrazine reacts with the thiocyanate with formation of phenylthiosemicarbazide and the unstable triphenylmethanehydrazobenzene described by Gomberg (Abstr., 1897, i, 623). From these experiments, the author concludes that the triphenylmethyl thiocyanate is a normal thiocyanate.

Benzoylthiocarbimide reacts with ethyl sodiomalonate, sodium formanilide, sodium phenoxide, or ethyl acetoacetate, and in each case sodium thiocyanate is produced. By the action of benzoylthiocarbimide on toluene in presence of aluminium chloride, a *compound*,

$$C_6H_4Me·CS·NHBz,$$

is obtained, which crystallises from alcohol in red prisms and melts at 135—136°. With phenetole under similar conditions, *p*-ethoxythiobenzamide, melting at 158°, is produced.

Benzoylthiocarbimide combines with hydrogen phosphide to form the *phosphocarbamide*, $NHBz·CS·PH_2$, as an orange precipitate, which melts at 155—157° and is readily soluble in alcohol but only sparingly so in benzene.

E. G.

3-Nitro- and 3-Amino-phenanthrene. By JULIUS SCHMIDT (*Ber.*, 1901, **34**, 3531—3535).—3-Nitrophenanthrene has been described by G. A. Schmidt (Abstr., 1879, i, 941) as γ-nitrophenanthrene and is reduced to 3-aminophenanthrene (Werner and Kunz, Abstr., 1901, i, 696, and G. A. Schmidt, *loc. cit.*); the *benzoyl* derivative of the base crystallises from alcohol in white, felted needles and melts at 213—214°; *3-phenanthrylurethane*, $C_{14}N_9·NH·CO_2Et$, crystallises from dilute alcohol in glistening, pale-yellow flakes and melts at 120—121°; *s-3-phenanthrylphenylcarbamide*,

$$C_{14}H_9·NH·CO·NHPh,$$

does not melt at 300°; when diazotised, the base is converted into 3-hydroxyphenanthrene (Pschorr, Abstr., 1900, i, 488). T. M. L.

Nitro-compounds of Anthragallol. II. By MAX BAMBERGER and FRITZ BÖCK (*Monatsh.*, 1901, **22**, 717—731. Compare Abstr., 1897, i, 576).—ψ-Nitroanthragallol is best prepared by the action of the dry vapour of nitric acid (from nitric and sulphuric acids) on anthragallol (compare *loc. cit.*). α-Nitroanthragallol is purified by crystallisation from a mixture of alcohol and benzene, from which it separates in dark ruby-red prisms containing 1 mol. of benzene; it forms a *triacetyl* derivative, $NO_2\cdot C_{14}H_4O_5Ac_3$, which crystallises in lemon-yellow needles melting at 233°.

Concentrated aqueous hydrochloric acid converts ψ-nitroanthragallol mainly into β-nitroanthragallol; but some chloronitroanthragallol is always simultaneously produced. In the presence of absolute alcohol and hydrogen chloride, ψ-nitroanthragallol yields monochloroanthragallol (Slama, Abstr., 1900, i, 181). α-Nitroanthragallol is formed from ψ-nitroanthragallol by the action of anhydrous formic acid.

ψ-Nitroanthragallol dissolves in pyridine, forming a steel-blue solution, which on heating becomes at first green and then reddish-brown. This solution contains the *pyridine* salt, $C_{14}H_8O_5,HNO_3,C_5NH_5$, which is obtained in indigo-blue crystals when acetone solutions of pyridine and ψ-nitroanthragallol are mixed. From acetyl chloride and ψ-nitroanthragallol is obtained a *compound*, $C_{16}H_{10}O_8NCl(?)$, in red crystals, which decomposes at 110° with evolution of acetyl chloride.

The view is expressed that ψ-nitroanthragallol is an additive product of nitric acid and anthragallol, whilst α- and β-nitroanthragallol are formed from it by the elimination of water. K. J. P. O.

Nitro-compounds of Anthragallol. III. By MAX BAMBERGER and FRITZ BÖCK (*Monatsh.*, 1901, **22**, 732—736. Compare preceding abstract).—The authors have attempted to prepare compounds analogous to ψ-nitroanthragallol, from anthragallol derivatives, in which the hydroxyl groups are wholly or partly replaced.

Anthragallolamine, $C_{14}H_5O_2(OH)_2\cdot NH_2$, yields with concentrated nitric acid a derivative crystallising in orange-yellow needles, which explode at 180°; it appears not to belong to the pseudo-series. Tribenzoylanthragallol, on nitration with vapour of nitric acid, did not yield a ψ-nitro-derivative; triacetylanthragallol, on the other hand, yielded such a compound.

The *dimethyl ether* of anthragallol, $OH\cdot C_{14}H_5O_2(OMe)_2$, prepared from anthragallol and methyl sulphate, crystallises in yellowish-green needles melting at 160°, and is soluble in potassium hydroxide with a red colour. It does not appear to be identical with two dimethyl ethers previously described by Perkin and Hummel (Trans., 1893, **63**, 1168). K. J. P. O.

Some Esters of Cholesterol and Phytosterol. By A. BÖMER and K. WINTER (*Zeit. Nahr.-Genussm.*, 1901, **4**, 865—888).—The authors have prepared the formic, acetic, propionic, butyric, and benzoic esters of both cholesterol and phytosterol, the latter being obtained from various oils, and melting at slightly different temperatures. Excepting the benzoate, which was prepared by heating the alcohols with benzoyl chloride in an open tube at 160°, the esters were obtained by heating the alcohols with five times their weight of the acids or their anhydrides in a sealed tube in the water-bath.

Full details are given of their chemical and crystallographical properties. The melting points of some of the esters of phytosterol, which differ with the source of the latter, are considerably higher than those of cholesterol, and in this way the two alcohols may be distinguished. The elementary composition of phytosterol whether prepared from cotton oil, ground nut oil, sesamé oil, colza oil, poppy oil, hempseed oil, linseed oil, or castor oil, is, however, the same; cholesterol has also the same composition (compare Abstr., 1899, ii, 191, 192, 259; 1900, ii, 178). L. DE K.

The Formation of Acid Chlorides by means of Thionyl Chloride. By HANS MEYER (*Monatsh.*, 1901, 22, 777—802. Compare Abstr., 1901, i, 407, 628).—*p*-Chloro- and *p*-bromo-benzoic acids only yield acid chlorides after long boiling with thionyl chloride; *p*-iodobenzoic acid reacts with thionyl chloride more readily. p-*Iodobenzamide*, formed from the acid chloride and ammonia, is a crystalline powder melting at 209°. *o*-Nitro- and *o*-hydroxyterephthalic chlorides are easily obtained; 2-*aldehydo*-5 : 6-*methoxybenzoyl chloride* (opianic chloride) is immediately formed from the acid and thionyl chloride at the ordinary temperature, and crystallises in yellow needles melting and decomposing at 83—84°. 8-Aldehydonaphthoic chloride is prepared with similar ease. The acid chloride obtained from benzoylbenzoic acid appears to be a mixture of the normal and pseudo-compounds, as with methyl alcohol it yields a mixture of two methyl esters. 1-*Hydroxy*-2-*naphthoic chloride* is a solid and with ammonia gives an *amide* which crystallises in needles melting at 190°. 2-Hydroxy-1-naphthoic and 3-hydroxy-2-naphthoic acids both yield chlorides; the *compound* from the latter acid is the more readily formed and crystallises in lemon-yellow needles melting at 192°; with methyl alcohol, it gives a *methyl* ester in yellow needles, melting at 72°, and with ammonia an amide (m. p. 188°). The groups OH and CO_2H in the para-position relatively to the CO_2H group hinder the formation of acid chlorides by thionyl chloride, whilst such groups as NO_2 and Br favour the formation of these compounds.

Although phloroglucinolcarboxylic acid (2 : 4 : 6-trihydroxybenzoic acid) does not react with thionyl chloride, the trimethyl ether readily yields an acid chloride; the monomethyl ether described by Herzig and Wenzel (Abstr., 1901, i, 473) also gives an acid chloride and must therefore be 2 : 6-dihydroxy-4-methoxybenzoic acid.

Terephthalic acid does not, but $\Delta^{1:4}$-dihydroterephthalic acid does react with thionyl chloride, yielding a dichloride. Dibromoadipic, α-dichloromuconic, and $\Delta^{\beta\gamma}$-dihydromuconic acids give dichlorides, whilst muconic acid does not react with thionyl chloride. *Piperic chloride*, prepared from piperic acid, crystallises in yellow needles melting at 180°, and the *methyl* ester prepared from it forms yellow leaflets melting at 140°. K. J. P. O.

The Three Cinnamic Acids. By ARTHUR MICHAEL [and, in part, WILLIAM R. WHITEHORNE] (*Ber.*, 1901, **34**, 3640—3666. Compare Liebermann, Abstr., 1890, 494, 620, and 1417; 1891, 832; 1892, 469 and 848; Erlenmeyer, Abstr., 1886, 945; 1891, 200).—The author has prepared three isomeric cinnamic acids in a state of purity, namely, cinnamic acid, m. p. 133°; *allo*cinnamic acid, m. p. 68°, and *iso*cinnamic acid, m. p. 36—37°. It is thought probable that the fourth isomeride described by Erlenmeyer as melting at 38—46° is a mixture of the *allo-* and *iso*-acids.

When β-bromo*allo*cinnamic acid, melting at 159°, is reduced with zinc dust and alcohol, the products are a minute quantity of cinnamic acid together with *allo*cinnamic acid, 75 per cent., and *iso*cinnamic acid, 25 per cent. The cinnamic acid is readily removed in the form of its calcium salt and the *allo-* and *iso*-acids may then be separated by crystallising their barium salts from methyl alcohol.

The following table of differences is given:

*iso*Cinnamic acid.	*allo*Cinnamic acid.
More readily soluble in most solvents.	—
Barium salt, with $2H_2O$, thin plates. Soluble in 0·8 part of methyl alcohol or in 4 parts of acetone.	Barium salt, with $3H_2O$, feathery needles. Soluble in 38 parts of methyl alcohol or in 124 parts of acetone.
Calcium salt, with $2H_2O$, soluble in 5 parts of acetone.	Calcium salt, with $3H_2O$, soluble in 50 parts of acetone.
Strontium salt, with $2H_2O$.	Strontium salt, with $3H_2O$.
Cadmium salt, anhydrous, soluble in 178 parts of water at 20°.	Cadmium salt, with $2H_2O$, soluble in 1010 parts of water at 20°.
Manganese salt, with $3H_2O$, soluble in cold water.	Manganese salt, with $2H_2O$; sparingly soluble even in hot water.

A small amount of the *iso*-acid is also obtained by the reduction of α-bromo*allo*cinnamic acid melting at 120°. β-Bromocinnamic acid (m. p. 134—135°), β-chloro*allo*cinnamic acid (m. p. 142°), β-iodocinnamic acid (m. p. 128°), and β-iodo*allo*cinnamic acid (m. p. 188°) all yield cinnamic acid and no trace of the *allo-* or *iso*-acid.

For the preparation of phenylpropiolic acid, the authors recommend boiling α-bromocinnamic acid with 20 per cent. alcoholic potassium hydroxide for 4 hours; when 2·5 mols. of alkali are used for each mol. of acid, the yield is 85 per cent. of the theoretical.

When phenylpropiolic acid is left in contact with concentrated hydriodic acid for 24 hours at 0°, the product consists of a mixture of *β-iodocinnamic acid* melting at 127—129° and readily soluble in most organic solvents, and *β-iodo*allo*cinnamic acid,* melting and decomposing at 186—188° and only sparingly soluble in cold organic solvents.

The addition of bromine to ethyl cinnamate has been studied under various conditions. In all cases, the product is a mixture of ethyl cinnamate dibromide melting at 74° and *ethyl cinnamate* allo*dibromide* melting at 28—30°, the best yield of the latter, namely, 54 per cent., is obtained when an excess of bromine is employed in carbon tetrachloride solution in the dark and at 0°. The *allo*-compound forms large, prismatic crystals readily soluble in the ordinary organic solvents, and is regarded as the normal additive product, whereas the ester melting at 74° is regarded as formed by intramolecular rearrangement. Methyl cinnamate and bromine also yield a mixture of methyl cinnamate dibromide melting at 117°, with an *allo*dibromide melting at 50—53° which is identical with the product obtained by Liebermann (*loc. cit.*) by the union of methyl*allo*cinnamate and bromine. The yield of *allo*-compound is greater when the combination occurs in the dark than in the light. The chief product obtained by the addition of bromine to cinnamic acid is the dibromide melting at 201° whilst only a small amount of *allo*dibromide melting at 91° is formed.

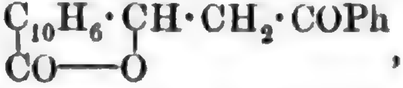
*allo*Cinnamic acid, when oxidised, yields the phenylglyceric acid melting at 121°. Ethyl cinnamate *allo*dibromide and silver benzoate yield the dibenzoate melting at 108—109°, which is also obtained from the ethyl ester dibromide melting at 74° (*Ber.*, 1879, **12**, 537).

The action of alcoholic sodium hydroxide on the two ethyl cinnamate dibromides has been studied. Three grams of *allo*dibromide (m. p. 28—30°) yield a mixture of 0·8 gram of α-bromo*allo*cinnamic acid melting at 120° and 1·2 grams of α-bromocinnamic acid melting at 131°, whilst 3 grams of the isomeric ester yield 0·1 gram of the α-bromo*allo*- and 1 gram of the α-bromo-cinnamic acid.

The following salts of phenylpropionic (hydrocinnamic) acid are described. Barium salt, large plates soluble in 33 parts of water at 27° and in 1000 of methyl alcohol at 25°. Calcium salt, soluble in 23 parts of water at 27° and 30 parts of acetone at 25°. Nickel salt, pale green precipitate, soluble in hot water. The nickel, manganese, cobalt, and copper salts are all moderately soluble in cold water. J. J. S.

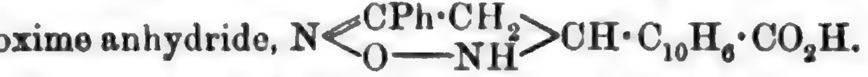
Kolbe's Reaction for the Formation of Aromatic Hydroxy-carboxylic Acids in Indifferent Solvents and its Relation to the Cryoscopic Behaviour of the Phenols in Benzene and in other Hydroxyl-free Solvents. By GIUSEPPE ODDO and E. MAMELI (*Gazzetta*, 1901, **31**, ii, 244—254).—The formation of hydroxy-acids by the action of carbon dioxide on the corresponding phenoxides often gives better yields when an indifferent solvent, such as toluene, light petroleum, or alcohol, is present; this action is very marked in the cases of the carboxy-acids of the α- and β-naphthols, and of phloroglucinol. The author finds that the more readily the hydroxy-acids are formed from phenols, the more readily do they decompose; salicylic acid, for example, is moderately stable, whilst the two naphthol-carboxylic acids and phloroglucinolmonocarboxylic acid readily decompose, even at the ordinary temperature. The less stable acids of the series react very readily with nitrous acid. From a study of the cryoscopic behaviour of: (1) *o*-cresol, which yields 5 per cent. of hydroxy-acid, in benzene and naphthalene; (2) *m*-xylenol, yielding 15 per cent. of hydroxy-acid, in benzene and naphthalene; (3) thymol, giving 50 per cent. of hydroxy-acid, in benzene and naphthalene; (4) carvacrol, which gives 15 per cent. of hydroxy-acid, in benzene; (5) α- and β-naphthols, which yield almost theoretical quantities of the corresponding hydroxy-acids, in benzene; (6) creosol, yielding 10 per cent. of hydroxy-acid, in benzene, and (7) guaiacol, which gives no trace of the corresponding hydroxy-acid, in benzene, the authors conclude that no definite relation exists between the cryoscopic behaviour of phenols in hydroxyl-free solvents and their greater or less capacity for yielding hydroxy-acids by Kolbe's method. T. H. P.

Condensation of Naphthalaldehydic Acid [8-Aldehydonaphthoic Acid] with Acetone and Acetophenone. By JOSEF ZINK (*Monatsh.*, 1901, **22**, 813—842).—8-Aldehydonaphthoic acid condenses with acetophenone in the presence of potassium hydroxide at 40—50° to yield *naphthalidomethyl phenyl ketone*, $COPh\cdot CH{:}CH\cdot C_{10}H_6\cdot CO_2H$, or



$\begin{array}{l} C_{10}H_6\cdot CH\cdot CH_2\cdot COPh \\ CO\text{———}O \end{array}$

, which forms white needles melting at 127°. With acetone, *naphthalidodimethyl ketone*, $C_{15}H_{12}O_3$, is formed, and crystallises in white leaflets melting at 76—78°. The *methyl* ester of naphthalidomethyl phenyl ketone, $C_{21}H_{16}O_3$, is prepared from the potassium salt and methyl iodide and crystallises in yellow needles melting at 90°. In acid solution, hydroxylamine and naphthalidomethyl phenyl ketone yield an *oxime*, $C_{20}H_{15}O_3N$, which crystallises in prisms melting at 123° and is decomposed into its components by hydrochloric acid. In alkaline solution, a *compound*, $C_{20}H_{16}O_3N_2$, is formed, which crystallises in needles melting at 165°, and is an oxamino-oxime anhydride,

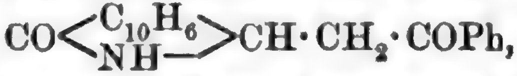


$N{<}\begin{smallmatrix} CPh\cdot CH_2 \\ O\text{——}NH \end{smallmatrix}{>}CH\cdot C_{10}H_6\cdot CO_2H$.

Naphthalidodimethyl ketone reacts with hydroxylamine both in alkaline and acid solution, forming *naphthalidodimethyl ketoxime*, the *hydrochloride*, $C_{15}H_{14}O_3NCl$, of which melts at 172—175°.

The *phenylhydrazone* of naphthalidomethyl phenyl ketone, $C_{26}H_{20}O_2N_2$, prepared from phenylhydrazine and the ketone, crystallises in needles melting at 155—160°, is insoluble in alkalis, and decomposed by hydrochloric acid into its components; by hydroxylamine hydrochloride it is converted into the oxime; the latter, with phenyl hydrazine, again yields the hydrazone. The *phenylhydrazone* of naphthalidodimethyl ketone, $C_{21}H_{18}O_2N_2$, crystallises in needles melting at 135—140°.

Ammonia converts naphthalidomethyl phenyl ketone into *phenacylnaphthalimidine*,

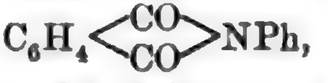


$CO{<}\begin{smallmatrix} C_{10}H_6 \\ NH\text{—} \end{smallmatrix}{>}CH\cdot CH_2\cdot COPh$,

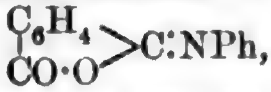
which crystallises in white needles melting at 163° and is converted by boiling hydrochloric acid and potassium hydroxide into an isomeric *compound*, $C_{20}H_{15}O_2N$, crystallising in lemon-yellow needles melting at 212°; as the latter is decomposed by prolonged boiling with potassium hydroxide with formation of acetophenone, it is represented by the formula $COPh\cdot CH{:}CH\cdot C_{10}H_6\cdot CO\cdot NH_2$. The imidine yields, with hydroxylamine, an *oxime*, $C_{20}H_{16}O_2N_2$, which forms rhombohedral crystals melting at 208°.

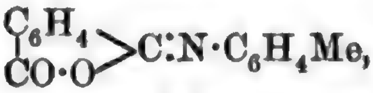
In an analogous manner, naphthalidodimethyl ketone yields *acetonylnaphthalimidine*, $C_{15}H_{13}O_2N$, crystallising in white needles melting at 142°; this gives an *oxime*, $C_{15}H_{14}O_2N_2$, crystallising in prisms and melting at 233°. K. J. P. O.

Action of Aromatic Amines on Phthalyl Chloride at different Temperatures. By MITSURU KUHARA and M. FUKUI (*Amer. Chem. J.*, 1901, **26**, 454—463).—When aniline reacts with phthalyl chloride at the ordinary temperature, *s*-phenylphthalimide,



$$C_6H_4{<}\begin{smallmatrix} CO \\ CO \end{smallmatrix}{>}NPh,$$

melting at 203°, is produced; if, however, an ethereal solution of phthalyl chloride, cooled to – 10°, is added to an ethereal solution of aniline at the same temperature, *a-phenylphthalimide*,  $\left.\begin{matrix}C_6H_4\\ CO\cdot O\end{matrix}\right\rangle C{:}NPh$, is formed, which crystallises in groups of white, microscopic needles, melts at 218°, and is slightly soluble in alcohol and readily so in hot glacial acetic acid. When this compound is heated with *o*-xylene at 140° in a sealed tube, it is converted into the *s*-isomeride, whilst if it is heated with water under these conditions, *s*-phenylphthalimide, aniline, and phthalic acid are produced. It is decomposed by alcoholic ammonia with formation of aniline and ammonium phthalate, whilst, as Laurent and Gerhardt have shown (*Jahresb. Chem.*, 1847—1848, 605), the *s*-compound is thereby converted into ammonium phenylphthalamate. When *s*-phenylphthalimide is boiled with a solution of barium hydroxide, phenylphthalamic acid is produced, but this substance is not formed when the *a*-isomeride is similarly treated. By the action of nitrous acid on phenylphthalamic acid, the *nitroso*-derivative, $CO_2H\cdot C_6H_4\cdot CO\cdot NPh\cdot NO$, is obtained, which forms slender, pale yellow crystals, dissolves readily in water or alcohol, and is very unstable.

a-o-Tolylphthalimide,  $\left.\begin{matrix}C_6H_4\\ CO\cdot O\end{matrix}\right\rangle C{:}N\cdot C_6H_4Me$, obtained in a manner similar to that by which *a*-phenylphthalimide is prepared, crystallises in silky needles, melts at 201°, and is easily soluble in hot alcohol. When kept in a fused state for 3 hours, it is converted into the *s*-isomeride, and if heated with water at 120° for 7 hours in a sealed tube, phthalic acid, *o*-toluidine, and *s*-*o*-tolylphthalimide are produced. By the action of barium hydroxide, it is decomposed into *o*-toluidine and phthalic acid. The *nitroso*-derivative of *o*-tolylphthalamic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot N(NO)\cdot C_6H_4Me$, closely resembles the corresponding compound of phenylphthalamic acid. E. G.

Pernitrososantonin and its Derivatives. By LUIGI FRANCESCONI and O. ANGELUCCI (*Gazzetta*, 1901, 31, ii, 302—312).—Although santonin resembles camphor in containing the group $\cdot CH_2\cdot CO\cdot$, it yields no *iso*nitroso-compound under conditions similar to those employed in the formation of *iso*nitrosocamphor. The authors have, however, succeeded in preparing a compound analogous to pernitrosocamphor.

Pernitrososantonin, $C_{15}H_{18}O_4N_2$, obtained by the action of amyl nitrite on santoninoxime, crystallises from ethyl acetate in pale yellow needles melting and decomposing at 190°. It is soluble in chloroform, acetone, and alcohol, and in chloroform solution has $[\alpha]_D$ $+169\cdot92°$. Dilute acids do not dissolve it and it is not altered by continued boiling with dilute hydrochloric acid; with Liebermann's reagent, it gives a greenish-blue coloration, whilst concentrated hydrochloric acid, ammonia, or potassium hydroxide decomposes it, giving santonin and nitrous oxide.

Santoninhydrazide, $(C_{15}H_{18}O_2N)_2$, prepared from the pernitroso-compound and hydrazine sulphate, crystallises from ethyl acetate in small, tetragonal octahedra, which melt and decompose at 254° and are readily soluble in alcohol or chloroform and, to a less extent, in ether; with hydrochloric acid, it yields santonin and hydrazine.

Santonin semicarbazone, $C_{16}H_{21}O_3N_3$, prepared from the pernitroso-compound, semicarbazide hydrochloride, and sodium acetate, separates from ethyl acetate in almost white crystals, which melt and decompose at 232° and are soluble in alcohol and, to a slight extent, in benzene or ether.

Dichlorosantonin, $C_{15}H_{18}O_3Cl_2$, obtained by distilling nitrosyl chloride into well-cooled santonin, crystallises from ethyl acetate in white, rhombic prisms, which melt and decompose at 160° and are soluble in alcohol or chloroform and, to a slight extent, in ether; in chloroform solution, it has $[\alpha]_D$ +230·08°.

From their results, the authors conclude that pernitrososantonin, and also the corresponding camphor derivative, have the constitution of a nitroso-oxime containing the grouping $\cdot CH_2\cdot \underset{\cdot}{C}\vdots NO\cdot NO$.

T. H. P.

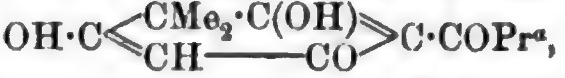
Filicyl-*n*-butanone. By Rudolf Boehm (*Annalen*, 1901, **318**, 230—245. Compare Abstr., 1898, i, 40; 1899, i, 804).—*Filicyl*-n-*butanone*, $C_{12}H_{16}O_4$, obtained by heating filicic acid or flavaspidic acid with zinc dust and sodium hydroxide solution (15 per cent.), crystallises from xylene in rhombic plates and melts at 95—97°. It is soluble in all the ordinary solvents excepting light petroleum and water and dissolves in solutions of the alkali hydroxides and carbonates. The dilute alcoholic solution has a strongly acidic reaction, and is excessively bitter to the taste. The ketone unlike filicic acid, does not yield the characteristic aniline reaction, but it develops an intense reddish-brown coloration with ferric chloride. The *ammonium* and *copper* salts are crystalline. The *hydrate*, $C_{12}H_{16}O_4,H_2O$, slowly separates from solutions of the ketone in dilute acetone. The ketone is hydrolysed into filicic and butyric acids after 12 hours' boiling with zinc dust and sodium hydroxide. The *phenylcarbamide*, $C_{12}H_{15}O_3\cdot O\cdot CO\cdot NHPh$, obtained by mixing its generators in dry benzene, crystallises in rhombic or hexagonal plates and melts at 115°.

Benzeneazofilicyl-n-*butanone*, $C_{12}H_{15}O_4\cdot N_2Ph$, produced from the ketone and an alcoholic solution of diazoaminobenzene, crystallises from alcohol in orange-yellow prisms and melts at 137°. *Benzenedisazofilicic acid*, $C_8H_8O_3(N_2Ph)_2$, prepared by substituting filicic acid for the above ketone in the preceding reaction, crystallises in dark red needles and melts at 209°.

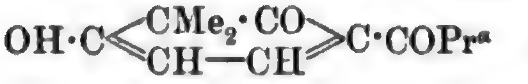
Phenylhydrazine and filicyl-*n*-butanone interact to form the *compound* $C_{24}H_{26}ON_4$; the substance crystallises in colourless prisms, melts at 183—184°, and is readily soluble in all the solvents except water.

Bromofilicyl-n-*butanone*, $C_{12}H_{15}O_4Br$, results from the bromination of the ketone in ethereal solution; it crystallises in colourless, hexagonal plates and melts at 85°. Filicyl-*n*-butanone, when treated with potassium hypobromite, undergoes simultaneous hydrolysis and bromination, the products being tetrabromofilicic and butyric acids. The former of these acids separates in colourless crystals and melts at 139—140°.

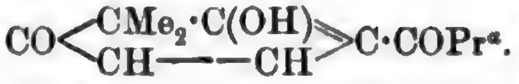
Filicyl-*n*-butanone must be represented by one or other of the following formulæ,



$\mathrm{OH\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe_2\cdot C(OH)}}{\mathrm{CH{-\!-\!-}CO}}{>}\mathrm{C\cdot COPr^{\alpha}}$,



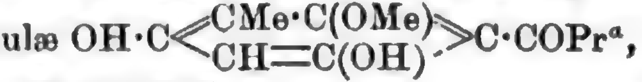
$\mathrm{OH\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe_2\cdot CO}}{\mathrm{CH{-}CH}}{>}\mathrm{C\cdot COPr^{\alpha}}$ or



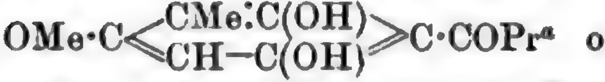
$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe_2\cdot C(OH)}}{\mathrm{CH{-\!-\!-}CH}}{>}\mathrm{C\cdot COPr^{\alpha}}$.

G. T. M.

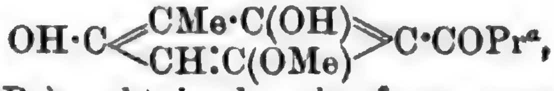
Aspidinol. By RUDOLF BOEHM (*Annalen*, 1901, **318**, 245—252. Compare Abstr., 1898, i, 40, and the preceding abstract).—The melting point of pure aspidinol is 156—161°, and not 143° as previously indicated; the substance is a ketone having one or other of the following formulæ



$\mathrm{OH\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe\cdot C(OMe)}}{\mathrm{CH{=}C(OH)}}{>}\mathrm{C\cdot COPr^{\alpha}}$,



$\mathrm{OMe\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe{:}C(OH)}}{\mathrm{CH{-}C(OH)}}{>}\mathrm{C\cdot COPr^{\alpha}}$ or



$\mathrm{OH\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{CMe\cdot C(OH)}}{\mathrm{CH{:}C(OMe)}}{>}\mathrm{C\cdot COPr^{\alpha}}$,

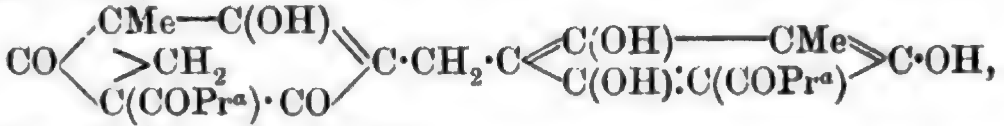
Dibenzoyl aspidinol, $OMe\cdot C_{11}H_{11}(OBz)_2$, obtained only from pure aspidinol by the Schotten-Baumann reaction, crystallises from alcohol in colourless prisms, melts at 108—109°, and is insoluble in solutions of the alkali hydroxides; it does not develop any coloration with ferric chloride.

Bromoaspidinol, $C_{12}H_{15}O_4Br$, produced by brominating aspidinol in chloroform, crystallises in plates and prisms and melts at 95—96°. It dissolves in the organic solvents and in aqueous solutions of the alkali hydroxides; with ferric chloride, it develops a dark green coloration.

Aspidinol, when heated with concentrated sulphuric acid for a few minutes on the water-bath, decomposes, yielding methylphloroglucinol and butyric acid. *Methoxydihydroxymethylbenzene*, $OMe\cdot C_6H_2Me(OH)_2$, and butyric acid are produced when aspidinol is digested for 10 hours with zinc dust and sodium hydroxide solution; the former substance crystallises from water in the monohydrated form, $C_8H_{10}O_3,H_2O$, and when condensed with diazoaminobenzene it combines with two diazo-residues, yielding the *compound* $OMe\cdot C_6Me(OH)_2(N_2Ph)_2$, which crystallises in scarlet needles and melts at 204°. Aspidinol itself combines with only one diazo-residue, giving rise to *benzeneazoaspidinol*, $C_{12}H_{15}O_4\cdot N_2Ph$, a compound crystallising from alcohol in scarlet needles and melting at 132°. G. T. M.

Constitution of Albaspidin and Flavaspidic and Filixic Acids. Two Noteworthy Reactions in the Phloroglucinol Series. By RUDOLF BOEHM (*Annalen*, 1901, **318**, 253—308. Compare Abstr., 1898, i, 40; 1899, i, 32, 804, and preceding abstracts).—Flavaspidic acid is now considered to have the formula $C_{24}H_{28}O_8$; it is obtained in two forms, the α-modification crystallising from methyl or ethyl alcohol in lemon-yellow prisms melting at 92°, and the β-modification separating from benzene, xylene, or acetic acid solutions in flattened plates melting at 156°. Both varieties of the acid, when subjected to the Schotten-Baumann reaction in the presence of sodium hydroxide, give rise to a small amount of a colourless, crystalline product which is soluble in alkali hydroxide solutions and melts at 143—144°. The β-modification yields only a *tribenzoyl* derivative when this reaction is repeated with potassium hydroxide; the product obtained in the form of an amorphous powder melts indefinitely at 150—160°, it is insoluble in alkali hydroxide solutions and develops a reddish-brown coloration with ferric chloride. *Diacetylflavaspidic acid*, prepared by the action of acetic anhydride on flavaspidic acid, crystallises from alcohol and melts at 142—143°; it is soluble in solutions of the alkali hydroxides and develops a coloration with ferric chloride. The *compound* $C_{24}H_{26}O_7$ is obtained by the action of acetic anhydride on flavaspidic acid; it melts at 157°.

Flavaspidic acid, when heated with zinc dust and sodium hydroxide solution, undergoes simultaneous hydrolysis and hydrogenisation, 2 mols. of water and 1 mol. of hydrogen being required for the complete decomposition of 1 mol. of the substance. Under these conditions, two-thirds of the flavaspidic acid decomposes into filicyl-*n*-butanone, filicic acid, dimethylphloroglucinol, and butyric acid, whilst the remainder of the acid yields trimethylphloroglucinol, methylphloroglucinol, and butyric acid. The following constitutional formula for flavaspidic acid,



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{CMe{-}C(OH)}\\ \;>\mathrm{CH_2}\\ \mathrm{C(COPr^{\alpha})\cdot CO}\end{array}\right\rangle\mathrm{C\cdot CH_2\cdot C}\left\langle\begin{array}{l}\mathrm{C(OH){-\!-\!-}CMe}\\ \mathrm{C(OH){:}C(COPr^{\alpha})}\end{array}\right\rangle\mathrm{C\cdot OH},$$

epitomises the foregoing results.

Benzeneazomethylphloroglucinyl-n-*butanone*, $C_{11}H_{13}O_4\cdot N_2Ph$, obtained by treating an alcoholic solution of flavaspidic acid with diazoaminobenzene, is also formed by adding benzenediazonium sulphate to the alkaline solution of the acid. The azo-compound crystallises from glacial acetic acid in scarlet needles and melts at 181—182°; it is insoluble in the ordinary organic solvents, but readily dissolves in solutions of the alkali hydroxides and carbonates.

Aminomethylphloroglucinol hydrochloride, $C_7H_9O_3N,HCl,2H_2O$, produced by reducing the preceding compound with stannous chloride, is isolated in the form of colourless or blue prisms, after removing the tin as sulphide and concentrating the solution in a vacuum over sulphuric acid; it melts indefinitely at 200—230°. At 55—60°, it loses water, yielding the anhydrous salt. The aqueous solution, when rendered alkaline with sodium hydroxide, develops a purple coloration which rapidly changes to blue.

Albaspidin is now represented by the formula $C_{25}H_{32}O_8$; it is shown to have the constitution of a methylenebisfilicyl-*n*-butanone by its partial synthesis from filicyl-*n*-butanone and formaldehyde. When condensed with diazoaminobenzene, albaspidin yields 2 mols. of benzeneazofilicyl-*n*-butanone, the linking methylene radicle being displaced by the azo-residues. Albaspidin, when condensed with phenylhydrazine, yields the *compound* $C_{37}H_{40}O_4N_4$; this product separates from benzene and light petroleum in colourless, rhombic crystals and melts at 242°; it is probably a pyrazole derivative.

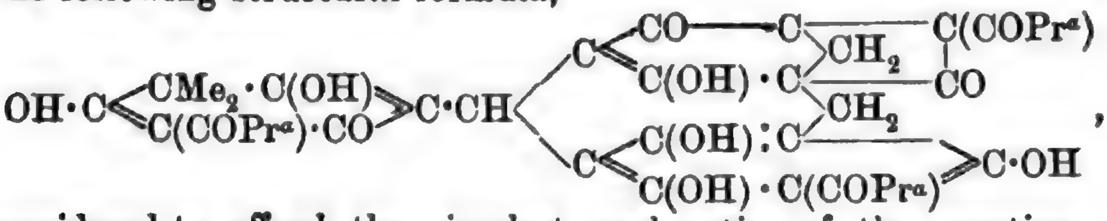
Albaspidin, when treated with zinc dust and sodium hydroxide, yields *n*-butyric and filicic acids, and an amorphous product which possibly contains 1 : 1 : 3-trimethylphloroglucinol.

Filixic acid, $C_{35}H_{38}O_{12}$, on boiling with alcohol for 3 hours, yields albaspidin; when heated with zinc dust and sodium hydroxide solution, it gives rise to filicyl-*n*-butanone, 1 : 3 : 5-trimethylphloroglucinol, *n*-butyric and filicic acids. By the action of diazoaminobenzene on filixic acid, *benzenedisazo-*1 : 3 : 5*-hydroxyphenyl* n*-butanone*,

$$(OH)_3\cdot C_6(N_2Ph)_2\cdot COPr^a,$$

is obtained; it crystallises from glacial acetic acid in red needles melting at 235°, the crystals contain $1C_2H_4O_2$, which is removed on heating at 100°.

The following structural formula,



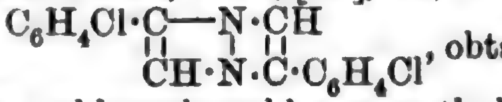
is considered to afford the simplest explanation of the reactions of filixic acid.

Methylenebis-dimethylphloroglucinol, $CH_2[C_6Me_2(OH)_3]_2$, prepared by condensing dimethylphloroglucinol with formaldehyde in dilute hydrochloric acid solution, crystallises from alcohol in needles melting at 252°; when heated with zinc dust and sodium hydroxide solution, it yields a mixture of di- and tri-methylphloroglucinols. The methylene radicle in this diphenylmethane derivative is again eliminated by the action of diazoaminobenzene in alcoholic solution with the formation of benzeneazodimethylphloroglucinol (m. p. 200°). G. T. M.

Euxanthic Acid. By Carl Graebe, R. H. Aders, and J. Heyer (*Annalen*, 1901, **318**, 345—365. Compare Abstr., 1901, i, 85).—The greater portion of the work has already been published.

Barium euxanthate, $Ba(C_{19}H_{17}O_{11})_2,9H_2O$, is a gelatinous, yellow precipitate obtained by treating the corresponding ammonium salt with barium chloride. The product of the acetylation of euxanthic acid with acetyl chloride consists of a mixture of the monoacetyl compound, and a derivative containing 3 or 4 acetyl groups. Ethyl euxanthate, when treated with acetyl chloride or acetic anhydride, yields a homogeneous product, *ethyl tetra-acetyleuxanthate*, $C_{19}H_{11}O_{10}EtAc_4$; this compound crystallises from alcohol in white needles and melts at 216°. The acyl and alkyl derivatives of euxanthic acid give rise to euxanthone when hydrolysed either with cold concentrated sulphuric acid or with water in sealed tubes at 150—180°. G. T. M.

Action of Alcoholic Ammonia on the ω-Bromine Derivatives of *p*-Chlorophenyl Methyl Ketone and *p*-Bromophenyl Methyl Ketone. By A. Collet (*Bull. Soc. Chim.*, 1901, [iii], **25**, 929—931).—2 : 5*-Di-*p*-chlorophenylpyrazine*,



$$\begin{array}{l} C_6H_4Cl\cdot C—N\cdot CH \\ \qquad\;\; \| \quad\;\; | \quad \| \\ \qquad\;\; CH\cdot N\cdot C\cdot C_6H_4Cl \end{array}$$

obtained by the action of alcoholic ammonia on *p*-chlorophenyl bromomethyl ketone, crystallises in slightly yellow, nacreous plates melting at 200—201°. 2 : 5*-Di-*p*-bromophenylpyrazine*, obtained in a similar manner from *p*-bromo-phenyl bromomethyl ketone, crystallises in brilliant, yellow needles melting at 235—236°. Both compounds are dissolved, without decomposition, by hot concentrated nitric acid; they are also dissolved by concentrated sulphuric acid with the production of a red coloration which disappears on dilution with water. N. L.

Derivatives of Acetophenone. By HANS RUPE, A. BRAUN, and KASIMIR VON ZEMBRUSKI (*Ber.*, 1901, **34**, 3522—3526).—*Acetyl*-m-*amino-acetophenone*, $NHAc\cdot C_6H_4\cdot COMe$, crystallises from dilute alcohol in white prisms or needles and melts at 128—129°; the *oxime*, $NHAc\cdot C_6H_4\cdot CMe\colon NOH$, separates from dilute alcohol in needles and melts at 192—194°. m-*Dimethylaminoacetophenone*, $NMe_2\cdot C_6H_4\cdot COMe$, boils at 148° under 13 mm. pressure and solidifies to a crystalline mass which melts at 42—43°; the *hydriodide*, $COMe\cdot C_6H_4\cdot NHMe_2I$, is sparingly soluble in water; the *hydrochloride* forms white needles; the *methiodide*, $COMe\cdot C_6H_4\cdot NMe_3I$, crystallises from water in broad tablets and melts at 200—201°; the *oxime*, $NMe_2\cdot C_6H_4\cdot CMe\colon NOH$, crystallises from dilute alcohol in white needles and melts at 78—79°. o-*Nitro*-p-*dimethylaminoacetophenone*, $COMe\cdot C_6H_3(NO_2)\cdot NMe_2$, crystallises from dilute alcohol in long, yellow needles with a steely lustre and melts at 149—150°. o-*Amino*-p-*dimethylaminoacetophenone hydrochloride*, $COMe\cdot C_6H_3(NH_2)\cdot NMe_2,HCl$, crystallises from hydrochloric acid in white needles; the *stannochloride* forms yellowish-brown flakes; the *platinichloride* forms brown flakes; the *base* is a yellow oil which boils at 220° under 52—53 mm. pressure and does not solidify on cooling; the *acetyl* derivative crystallises from water in white needles and melts at 146—148°. T. M. L.

Chromophore Groups. By HANS RUPE and D. WASSERZUG (*Ber.*, 1901, **34**, 3527—3531).—m-*Nitrobenzylidene*-m-*nitroacetophenone*, $NO_2\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot C_6H_4\cdot NO_2$, crystallises from acetic acid in yellow needles and melts at 210°. m-*Aminobenzylidene*-m-*aminoacetophenone*, $NH_2\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot C_6H_4\cdot NH_2$, is a yellow powder; the *hydrochloride* forms prismatic crystals; the *diacetyl* derivative crystallises from alcohol in small, white needles and melts at 150°; the base forms a series of tetrazo-dyes containing the complex $\cdot N_2\cdot C_6H_4\cdot CO\cdot CH\colon CH\cdot C_6H_4\cdot N_2\cdot$. p-*Dimethylaminobenzylidene*-m-*nitroacetophenone*,

$$NMe_2\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot C_6H_4\cdot NO_2,$$

crystallises from acetic acid in minute, red needles and melts at 165°. p-*Dimethylaminobenzylidene*-m-*aminoacetophenone*,

$$NMe_2\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot C_6H_4\cdot NH_2,$$

forms a white, crystalline *hydrochloride* and a *platinichloride* which crystallises from hot water in large, brownish-red octahedra. 3 : 4-*Dihydroxybenzylidene*-m-*nitroacetophenone*, $C_6H_3(OH)_2\cdot CH\colon CH\cdot CO\cdot C_6H_4\cdot NO_2$, crystallises from dilute alcohol, melts at 217°, and with mordants forms a very stable dye; the *diacetyl* derivative forms minute, white, silky needles and melts at 179°; the *diethyl* ether crystallises from a mixture of alcohol and ether in minute, yellowish needles and melts at 103°.

T. M. L.

Condensation Products of Phenylacetone [Benzyl Methyl Ketone] with Benzaldehyde. By GUIDO GOLDSCHMIEDT and HANS KRCZMAŘ (*Monatsh.*, 1901, **22**, 659—669. Compare Abstr., 1898, i, 31, and 1899, i, 140).—Benzyl methyl ketone and benzaldehyde condense under different conditions to form two isomeric ketones, $C_{16}H_{14}O$ (*loc. cit.*). In this paper, the constitution of the two ketones is discussed, and the conclusion drawn that the ketone melting at 71°, obtained by using potassium hydroxide as condensing agent, is benzyl cinnamenyl ketone,

$CH_2Ph\cdot CO\cdot CH\colon CHPh$, whilst the ketone melting at 53°, obtained when hydrogen chloride is used, is stilbyl methyl ketone,

$$CHPh\colon CHPh\cdot COMe.$$

By reducing the ketone which melts at 53° (or the ketone, $C_{16}H_{15}OCl$, *loc. cit*), with sodium amalgam, a *ketone* [*dibenzyl methyl ketone*], $C_{16}H_{16}O$, is obtained as a yellowish oil which boils at 311—312° and solidifies in a freezing mixture; the *oxime*, $C_{16}H_{17}ON$, crystallises in white needles melting at 134°.

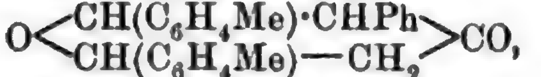
On reducing the ketone, which melts at 71°, with sodium amalgam, an oily ketone, boiling at 234—238° under 79 mm. pressure, is formed, and proves to be benzyl phenylethyl ketone (compare Spiegel, *Annalen*, 1883, **219**, 34); the *oxime*, $C_{16}H_{17}ON$, melts at 120°.

The ketone, $C_{22}H_{18}O$ (m. p. 86°), prepared by Goldschmiedt and Knöpfer (Abstr., 1900, i, 35) from dibenzyl ketone and benzaldehyde, is stilbyl benzyl ketone and not 1 : 2-diphenyltetrahydro-β-naphthenone as previously suggested. K. J. P. O.

Condensation of Phenylacetone [Benzyl Methyl Ketone] with Aromatic Aldehydes. By Guido Goldschmiedt and Hans Krczmař (*Monatsh.*, 1901, **22**, 749—759. Compare Abstr., 1898, i, 31; 1899, i, 140; 1900, i, 35; and preceding abstract).—Phenylacetone and *p*-tolualdehyde, when shaken together for several days in the presence of dilute alcoholic potassium hydroxide, yield two substances, *p*-methylcinnamenyl benzyl ketone and 2 : 6-di-*p*-tolyl-3-phenyltetrahydro-1 : 4-pyrone.

Benzyl p-*methylcinnamenyl ketone*, $CH_2Ph\cdot CO\cdot CH\colon CH\cdot C_6H_4Me$, crystallises in prisms melting at 115°, and with bromine gives *benzyl α*-p-*methyldibromocinnamenyl ketone*, $C_{17}H_{16}OBr_2$, which crystallises in needles melting at 106°. On warming an alcoholic solution of this substance, it is transformed into an isomeric *β-compound*, which crystallises in needles melting at 89°. With hydroxylamine hydrochloride, benzyl *p*-methylcinnamenyl ketone yields a *compound*, $C_{17}H_{17}ON$, which crystallises in needles melting at 147°, and is probably not an oxime, but 3-benzyl-5-*p*-tolyl*iso*oxazole.

2 : 6-*Di*-p-*tolyl-3-phenyltetrahydro*-1 : 4-*pyrone*,



$$O<\begin{matrix}CH(C_6H_4Me)\cdot CHPh\\ CH(C_6H_4Me)—CH_2\end{matrix}>CO,$$

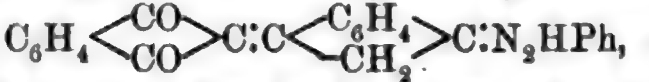
crystallises in needles melting at 153—154°.

p-*Methoxycinnamenyl benzyl ketone*, $CH_2Ph\cdot CO\cdot CH\colon CH\cdot C_6H_4\cdot OMe$, prepared from anisaldehyde and phenylacetone, crystallises in leaflets melting at 98—100°, and with bromine yields a *dibromide*, $C_{12}H_{16}O_2Br_2$, which melts at 116—117°. *Benzyl* p-*methoxybromocinnamenyl ketone*, $C_{12}H_{15}O_2Br$, formed on boiling the dibromide with alcohol, crystallises in needles melting at 85°. On treating the ketone with hydroxylamine, a *compound*, $C_{17}H_{17}O_2N$, is formed, which melts at 97—98°.

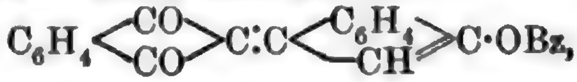
Benzyl 3 : 4-*methylenedioxycinnamenyl ketone*,

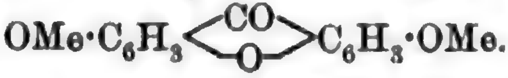
$$CH_2Ph\cdot CO\cdot CH\colon CH\cdot C_6H_3\colon O_2\colon CH_2,$$

prepared from piperonal and phenylacetone, crystallises in prisms melting at 100—102°; with bromine, a *dibromide*, $C_{17}H_{14}O_3Br_2$, is obtained as needles melting at 135°, and with hydroxylamine, a *compound*, $C_{17}H_{15}O_3N$, which melts at 137°. K. J. P. O.

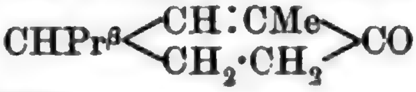
Derivatives of Anhydrobisdiketohydrindene. By E. HOYER (*Ber.*, 1901, **34**, 3269—3274).—*Anhydrobisdiketohydrindene phenylhydrazone*,  $\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C{:}C}<\begin{matrix}\mathrm{C_6H_4}\\\mathrm{CH_2}\end{matrix}>\mathrm{C{:}N_2HPh}$, crystallises from chloroform in lustrous, blood-red needles and melts and decomposes at 236°. The *benzylidene* derivative, $\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C{:}C}<\begin{matrix}\mathrm{C_6H_4}\\\mathrm{C(CHPh)}\end{matrix}>\mathrm{CO}$, crystallises from glacial acetic acid in yellowish-red, lustrous needles and melts at 205°; the analogous *cinnamylidene* derivative, $C_{27}H_{16}O_3$, separates from the same solvent in scarlet spangles and melts at 243°; the p-*methoxybenzylidene* compound forms small, lustrous, reddish-brown needles melting at 242°.

The *methyl ether*, $\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C{:}C}<\begin{matrix}\mathrm{C_6H_4}\\\mathrm{CH}\end{matrix}>\mathrm{C{\cdot}OMe}$, derived from the isodynamic form of anhydrobisdiketohydrindene and formed on saturating a methyl alcoholic solution of the latter with hydrogen chloride, crystallises in dark-red, lustrous needles melting at 196°; the *ethyl* ether crystallises from alcohol in reddish-brown needles melting at 159°, and the *propyl* ether from acetone on diluting with water in dark-red, lustrous needles melting at 135°. When the propyl ether is boiled with bromine and a little iodine in glacial acetic acid solution, dibromoanhydrobisdiketohydrindene (Wislicenus and Kötzle, Abstr., 1889, 1067), and not a bromo-derivative of the ether, is formed; it melts at 251°, not at 241—242°, and is only obtained with difficulty by brominating anhydrobisdiketohydrindene according to the directions formerly given (*loc. cit.*), although formed quantitatively by boiling with bromine and a little iodine in glacial acetic acid solution.

Benzoylanhydrobisdiketohydrindene,  $\mathrm{C_6H_4}<\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}>\mathrm{C{:}C}<\begin{matrix}\mathrm{C_6H_4}\\\mathrm{CH}\end{matrix}>\mathrm{C{\cdot}OBz}$, crystallises from benzene in dark red needles and melts and decomposes at 210—214°. W. A. D.

Methylation of Euxanthone and Alizarin with Dimethyl Sulphate. By CARL GRAEBE and R. H. ADERS (*Annalen*, 1901, **318**, 365—370).—Euxanthone, when treated at the ordinary temperature with dimethyl sulphate and sodium hydroxide, yields the yellow monomethyl ether described by Kostanecki, and a small quantity of the *dimethyl* ether,  $\mathrm{OMe{\cdot}C_6H_3}<\begin{matrix}\mathrm{CO}\\\mathrm{O}\end{matrix}>\mathrm{C_6H_3{\cdot}OMe}$. The latter compound is more conveniently prepared by methylating the sodium derivative of the former product with the same reagents on the water-bath; it separates from dilute alcohol or light petroleum in colourless crystals and melts at 149·5°. This compound has already been obtained, but only in an impure state (Graebe and Ebrard, Abstr., 1882, 1301). A colourless *monomethyl* ether of euxanthone is produced by hydrolysing the dimethyl derivative with hot concentrated sulphuric acid (90 per cent.); it resembles the corresponding monoethyl compound and dissolves in alcohol, chloroform, or solutions of the alkali hydroxides and melts at 240° (compare Herzig, Abstr., 1891, i, 1349).

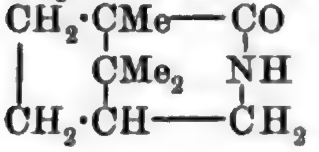
When heated with zinc dust, the dimethyl ether yields a very small amount of a red substance melting at 90—100°, and probably consisting of xanthene. The 2-methyl ether of alizarin is readily prepared from dimethyl sulphate in the presence of an alkali hydroxide. It was, however, not found possible to produce the dimethyl ether even by treating the red, insoluble *sodium* derivative of the monomethyl compound with boiling dimethyl sulphate or with methyl iodide at 180°. G. T. M.

Derivatives of Camphor. By MATTEO SPICA (*Gazzetta*, 1901, **31**, ii, 286—288).—The author has obtained further evidence in support of the formula  $CHPr^{\beta}<{CH:CMe \atop CH_2\cdot CH_2}>CO$ for *iso*camphor by converting it into *m*-cymene.

The reduction of the oxime of *iso*camphor in alcoholic solution by means of sodium yields the corresponding *amine*, $C_{10}H_{21}N$, which is a colourless oil boiling at 201° under the ordinary pressure, and having a characteristic odour. The hydrochloride of the amine, when treated with sodium nitrite, yields tetrahydro*iso*camphor, whilst with potassium cyanate, the corresponding *carbamide*, $NH_2\cdot CO\cdot NH\cdot C_{10}H_{19}$, is obtained in the form of colourless crystals melting at 155°. On heating the phosphate of the amine, it yields a hydrogenised *hydrocarbon*, which is a yellowish liquid boiling at 169—171°. On treating this hydrocarbon with excess of an acetic acid solution of hydrogen bromide, it was found that the products, volatile in a current of steam, gave, on oxidation by the methods given by Wallach and by Baeyer, certain acids, which, by their melting points, are found to be identical with those yielded by the oxidation of *m*-cymene. The question is being further investigated with larger quantities of material.

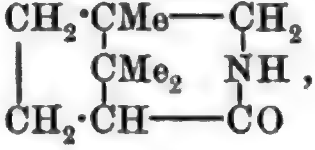
T. H. P.

Electrolytic Reduction of Camphorimide. By JULIUS TAFEL and KARL ECKSTEIN (*Ber.*, 1901, **34**, 3274—3286).—Camphorimide is best prepared by heating camphoric acid with 25 per cent. aqueous ammonia for 6 hours at 180°, and melts at 248° (uncorr.), not at 244—245° as formerly stated; its rotatory power depends on the concentration of its solutions. A solution of 20 grams in 100 c.c. of chloroform gave $[\alpha]_D$ +5·45° at 23°; of 10 grams, $[\alpha]_D$ +4·3° at 23°; and of 5 grams, $[\alpha]_D$ +1·55° at 23°; with 2·5 grams, a rotation was no longer discernible. When a solution of the imide in 65 per cent. sulphuric acid is electrolysed, a mixture of α- and *β-camphidones*,



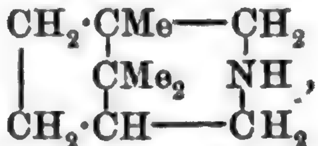
$$\begin{array}{l} CH_2\cdot CMe—CO \\ \quad | \quad CMe_2 \quad NH \\ CH_2\cdot CH—CH_2 \end{array}$$

and



$$\begin{array}{l} CH_2\cdot CMe—CH_2 \\ \quad | \quad CMe_2 \quad NH \\ CH_2\cdot CH—CO \end{array}$$

, and *camphidine*,



$$\begin{array}{l} CH_2\cdot CMe—CH_2 \\ \quad | \quad CMe_2 \quad NH \\ CH_2\cdot CH—CH_2 \end{array},$$

is obtained; as the two former are not further reduced on electrolysis in sulphuric acid solution, the camphidine must be formed by the simultaneous reduction of the two carbonyl groups of the imide.

α-*Camphidone* differs from its isomeride in yielding a sparingly soluble *picrate*, which crystallises from water in long, thin, anhydrous needles, melts at 190—192°, and on decomposition with alkali yields the pure base; the latter melts at 230—232°, boils at 295° under 762 mm. pressure, crystallises from water, acetone, or light petroleum, and has $[\alpha]_D$ $-37{\cdot}2°$ at 20° in a 10 per cent. benzene solution. It yields a sparingly soluble *platinichloride*, *phosphomolybdate*, *phosphotungstate*, *bismuthoiodide*, and *mercurichloride*. It is not acted on by reducing agents, such as sodium in amyl alcoholic solution, or by boiling alcoholic sodium hydroxide, or aqueous barium hydroxide at 180°; the lactam ring is thus extraordinarily stable, and very different from that existing in the pyrrolidones.

β-Camphidone, purified initially by means of its picrate, and subsequently by crystallising from water, melts at 225°, and boils at 307—308° under 757 mm. pressure; it melts when heated with water, then dissolves to form a *hydrate*, $C_{10}H_{17}ON,H_2O$, which crystallises in long, colourless needles. α-Camphidone has $[\alpha]_D$ $+66{\cdot}5°$ at 20° in a 10 per cent. benzene solution; like the β-compound, it is indifferent to reducing and hydrolytic agents, and yields similar double salts. The *picrate* crystallises from water or alcohol in stout, yellow needles and melts at 135—136°.

Camphidine forms a soft, crystalline mass of strongly camphor-like odour, melts at 186° (uncorr.), and boils at 209° (corr.) under 755 mm. pressure; in 10 per cent. benzene solution, it has $[\alpha]_D$ $+23{\cdot}9°$ at 20°. Its aqueous solution is strongly alkaline; the *hydrochloride* is easily soluble in water and alcohol, and separates from the latter on adding ether in pike-shaped crystals; the *nitrate* crystallises from alcohol in needles melting and decomposing at 199° (uncorr.), and the *platinichloride* from water in thin, rectangular plates. The *picrate* is easily soluble in warm water. *Acetylcamphidine*, $C_{12}H_{21}ON$, forms a soft, crystalline mass, melts between 30° and 40° and boils at 290—291°; *nitrosocamphidine*, $C_{10}H_{18}ON_2$, crystallises from warm alcohol and gives Liebermann's reaction. *Camphidinephenylthiocarbamide*,

$$C_{10}H_{19}N{\cdot}C_6H_5{\cdot}NCS,$$

crystallises from alcohol in silky nodules and melts at 142—145° (uncorr.). With bromine in hydrobromic acid solution, camphidine yields a reddish-yellow perbromide. W. A. D.

New Crystalline Component of Bergamot Oil. By HUGO VON SODEN and WILHELM ROJAHN (*Chem. Centr.*, 1901, ii, 930; from *Pharm. Zeit.*, **46**, 778—779).—The residue left after distilling bergamot oil contains not only bergapten but also a crystalline compound, *bergaptin*, which probably belongs to the aromatic series. It crystallises from light petroleum in leaflets, from ether in plates which resemble cubes, is easily soluble in alcohol, ether, or chloroform, and combines with bromine. The free acid obtained by treating bergaptin with potassium hydroxide and acidifying with sulphuric acid changes spontaneously into bergaptin. Bergaptin contains neither phenolic nor methoxy-groups, but its carbon chain probably resembles that of coumarin. E. W. W.

Empyreaumatic Oil of Juniper. Cadinene. By CATHELINEAU and JEAN HAUSSER (*Bull. Soc. Chim.*, 1901, [iii], **25**, 931—933. Compare Abstr., 1901, i, 283).—The largest yield—about 8 per cent.—of cadinene hydrochloride is obtained from *unrectified* empyreaumatic oil of juniper, the possible decomposition of cadinene by heat being thus avoided. Full details of the process employed and the modifications introduced by the authors are given in the paper. N. L.

Citrapten. By ERNST SCHMIDT [with ADLUNG] (*Chem. Centr.*, 1901, ii, 809—810; from *Apoth.-Zeit.*, 16, 619—620. Compare Theulier, Abstr., 1901, i, 218).—Citrapten, $C_9H_4O_2(OMe)_2$, obtained from the residue left after distilling lemon oil, crystallises in colourless needles or prisms, melts at 146—147°, sublimes easily, dissolves in alcohol forming a solution with a blue fluorescence, and is soluble in chloroform, slightly so in boiling water, ether, or light petroleum, and insoluble in cold dilute potassium hydroxide solution. The *nitro*-derivative crystallises in yellowish needles. The *dibromide*, $C_{11}H_{10}O_4Br_2$, forms yellowish needles, and melts at 250—260°. Citrapten is an acid anhydride or lactone and dissolves slowly in boiling dilute potassium hydroxide solution, but the acid which is precipitated from the alkaline solution on acidification is quickly reconverted into citrapten. Citrapten appears to be related to the dihydroxycoumarins and to be a derivative of phloroglucinol isomeric with dimethylæsculetin and dimethyldaphnetin. When fused with potassium hydroxide, it forms phloroglucinol and probably acetic acid. A *methyl ester*, prepared by the action of methyl iodide and sodium hydroxide on citrapten, forms colourless crystals, has acid properties, and melts at 215°.

A phenol, melting at 89°, was also isolated from the lemon oil residue. E. W. W.

Essential Oils of Neroli and Petit Grain distilled in 1901. By PAUL JEANCARD and C. SATIE (*Bull. Soc. Chim.*, 1901, [iii], 25, 934—936).—A number of specimens of oil of neroli and of petit grain distilled in 1901 after the severe winter of 1900—1901 were examined, and the analytical results compared with those yielded by specimens distilled in 1899 after a mild winter (Abstr., 1900, i, 511). The sp. gr., rotatory power, solubility in alcohol, saponification numbers (hot and cold), esters, surface tension, and specific viscosity were determined. The sp. gr. of oil of neroli is slightly higher this year than previously, whilst the reverse is the case with oil of petit grain; the other figures show little variation. N. L.

Storax. By LEOPOLD VAN ITALLIE (*Chem. Centr.*, 1901, ii, 856—857; from *Ned. Tijd. Pharm.*, 13, 225—235).—The resin alcohol of storax storesinol, $C_{16}H_{26}O_2$, melts at 156—161°, has $[\alpha]_D$ +13°, is soluble in the lower alcohols, ether, chloroform, acetone, carbon disulphide, benzene or glacial acetic acid, but is insoluble in light petroleum. Its solution in concentrated sulphuric acid is red and has a green fluorescence. It dissolves in a 1 per cent. solution of sodium or potassium hydroxide, but is precipitated by excess of the alkali and is attacked with difficulty by molten alkalis, forming acetic and salicylic acids. By the action of nitric acid, it yields oxalic and picric acids and on distillation with zinc dust, gives benzene, toluene, and phenol. Neither an oxime nor a phenylhydrazone could be prepared. Mylius' styrogenin, $C_{26}H_{40}O_3$, prepared by treating storesinol with sulphuric acid, crystallises in colourless leaflets which show only slight polarisation; it is odourless, melts above 360 and is soluble in chloroform, benzene or phenol, and readily so in hot alcohol but insoluble in ether or cold alcohol. By the action of hydriodic acid on styrogenin a *compound*, $C_{16}H_{26}O_3$, is formed which crystallises in colourless leaflets and melts at about 280°.

Styrene is actually contained as such in storax and is not formed during the distillation in steam. A good storax contains about 2·4 per cent. insoluble in ether, 23·1 of free cinnamic acid, 14·0 of water, 22·5 of aromatic esters, 2·0 of styrene and vanillin, and 36·0 of resin, and gives an acid number 81, saponification number 179, ester number 98, and saponification number of mixture of esters and styrol 209. The total cinnamic acid is 47·3 per cent., the combined acid being 24·2, occurring partly in the resin and partly in the aromatic esters. E. W. W.

American Storax. By LEOPOLD VAN ITALLIE (*Chem. Centr.*, 1901, ii, 857; from *Ned. Tijd. Pharm.*, **13**, 257—266).—American storax, prepared from *Liquidambar styraciflua*, L., is obtained in the form of a sticky, grey mass containing white, crystalline portions mixed with fragments of wood and bark. Its composition does not differ essentially from that of Asiatic storax. Coumarin, vanillin, styracin, phenylpropyl cinnamate, styrene, and an alcohol *styresinol*, $C_{16}H_{26}O_2$, have been isolated from it. Styresinol resembles storesinol in all its properties and may prove to be identical with it, but it has a specific rotatory power $[\alpha]_D$ +52°, whilst that of storesinol is +13°30′.

E. W. W.

Extraction of all the valuable Constituents from Digitalinum Germanicum. By HEINRICH KILIANI (*Ber.*, 1901, **34**, 3561—3562. Compare Abstr., 1891, 576; 1892, 1482; 1896, i, 58, 180). —Digitonine and *Digitalinum verum* can be simultaneously obtained from *Digitalinum germanicum* by precipitating the alcoholic extract with ether and working up the solution for *Digitalinum verum* and the precipitate for digitonin. For this purpose, the liquid is evaporated in a vacuum, the syrup dissolved in water, and all resinous matter removed by ether. The thick jelly of *Digitalinum verum* is then filtered off and washed with 5 per cent. alcohol. The filtrate contains digitalein.

The precipitate is dissolved by warming with 85 per cent. alcohol, and the digitonin then separates out on cooling. A. H.

Digitonin and Digitogenic Acid. By HEINRICH KILIANI and B. MERK (*Ber.*, 1901, **34**, 3562—3577. Compare Abstr., 1892, 1483). —Digitogenin is best prepared by heating an alcoholic solution of digitonin with 2 parts of concentrated hydrochloric acid at 100° and may be recrystallised by adding boiling water to its solution in boiling 95 per cent. alcohol until it becomes opalescent and then allowing it to cool. By the action of zinc and sulphuric acid in acetic acid solution, it is converted into a *compound*, $C_{30}H_{50}O_7$, which crystallises in colourless needles melting at 197—198°.

Digitogenic acid is best prepared by the oxidation of digitonin in acetic acid solution with chromic acid mixture. It is converted by nitric acid into two crystalline acids containing nitrogen. The more sparingly soluble of these "N-*acid* I," $C_{22}H_{28}O_8N_2$, or $C_{22}H_{30}O_8N_2$, sinters at 225° and melts and decomposes at 242°. The *barium* salt, $C_{22}H_{26}O_8N_2Ba,8H_2O$, is crystalline and sparingly soluble in water. The more soluble "N-*acid* II," $C_{44}H_{64}O_{15}N$, crystallises with $4H_2O$ in slender needles, becomes black at 250°, and melts at 261—263°. The *zinc* salt, $C_{44}H_{60}O_{15}NZn_2$, crystallises well with 8 or $9H_2O$, and is more readily soluble in cold than in hot water. The formation of a substance of this high molecular weight is either due to anhydride formation, or to the fact that the molecular weight of digitonin is higher than has been supposed.

Acetyldigitogenic acid, $C_{28}H_{43}O_8Ac$, is prepared by the action of acetic anhydride and crystallises with $1H_2O$ in needles which soften at 162—165°. Acetyl chloride yields a compound melting at 92° which has not been investigated.

Digitogenic acid yields two oximes; the *a-oxime*, $C_{28}H_{45}O_8N$, melts at 175°, but its composition differs from that assigned to it by Kiliani and Bazlen (Abstr., 1895, i, 65). The *magnesium* salt has the composition, $C_{28}H_{43}O_8NMg,5H_2O$. The *β-oxime* has the same composition as the α-compound, but melts at 105°. Digitoic acid, which is formed from digitogenic acid with loss of carbon monoxide, also yields a *monooxime*, $C_{27}H_{45}O_7N$, which crystallises in plates, softens at 234°, and melts at 244°. Digitogenic acid, therefore, probably contains two ketonic groups, only one of which reacts directly with hydroxylamine. Digitic acid, prepared from oxydigitogenic acid by oxidation with potassium permanganate in alkaline solution, after having been previously boiled with neutral permanganate, was found to be converted by boiling dilute sulphuric acid into a new acid, whilst no other sample of the acid underwent a similar change. In order to throw light on this abnormality, similar experiments have been carried out with digitogenic acid. When the aqueous solution of a salt of this acid is boiled, one portion of the acid is converted into β-digitogenic acid, whilst a second portion is decomposed with formation of digitoic acid. When the acid is boiled with dilute sulphuric acid, a portion of it is also converted into β-digitogenic acid, and a second portion is decomposed with formation of a new substance, *gitonic acid*, $C_{26}H_{44}O_6$, which softens at 220° and melts at 227°. The *magnesium* salt, $C_{26}H_{42}O_6Mg$, crystallises in needles.

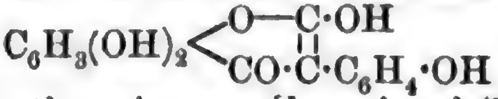
When digitogenic acid is oxidised by potassium permanganate at 100° it yields about 5—10 per cent. of the acid, $C_9H_{14}O_4$, or $C_{18}H_{28}O_8$, previously described by Kiliani (Abstr., 1893, i, 665). The monopotassium salt is dimorphous, crystallising in needles or compact, warty aggregations. A. H.

Identity of Digitoflavone with Luteolin. By HEINRICH KILIANI and O. MAYER (*Ber.*, 1901, **34**, 3577—3578).—The digitoflavone obtained by Fleischer and Fromm (Abstr., 1899, i, 631) from *Digitalis* leaves is, as suggested by Diller and Kostanecki (Abstr., 1901, i, 476), identical with luteolin. The tribenzoate obtained by Fleischer's method melts at 200—201°, whilst Fleischer's compound melted at 219°. A tetrabenzoate can be prepared by Deninger's method (Abstr., 1895, i, 461), and this is identical with that obtained by A. G. Perkin (Trans., 1896, **69**, 206) from luteolin. Its dyeing properties also agree with those of luteolin. A. H.

Scutellarin, a New Substance in Scutellaria and other Labiatæ. By Hans Molisch and Guido Goldschmiedt (*Monatsh.*, 1901, **22**, 679—699).—When the leaves of *Scutellaria altissima* are boiled with 1 per cent. hydrochloric acid, their lower sides become covered with microscopic crystalline aggregates. Crystals of the same substance, scutellarin, separate when the aqueous extract of the leaves is acidified. It is found chiefly in the leaves; it occurs in *Scutellariæ*, and in some other *Labiatæ*, as *Galeopsis tetrahit* and *Tencrium chamædrys.*

Scutellarin, $C_{21}H_{20}O_{12},2\frac{1}{2}H_2O$, is prepared by extracting the leaves and flowers of the plant with ten times the quantity of water and acidifying the extract with concentrated hydrochloric acid; the yield is less than 1 per cent. The acid filtrate from the scutellarin contains cinnamic and fumaric acids. Scutellarin crystallises in pale yellow needles, which darken at 200°, but do not melt at 310°. Lead acetate gives a red precipitate with the alcoholic solution, and ferric chloride an intense green coloration which becomes red on heating. Oxidising agents (chlorine, water, &c.) give an immediate green colour. Alkalis, ammonia, and alkali carbonates dissolve it with a deep yellow colour; these solutions reduce ammoniacal silver nitrate and Fehling's solution; acids reprecipitate scutellarin. Concentrated sulphuric acid dissolves it with a yellow colour. From the solution or suspension in acetic acid, concentrated mineral acids throw down deep yellow or orange, crystalline salts. The *acetyl* derivative melts and decomposes at 267°. When fused with potash, *p*-hydroxybenzoic acid and a substance, which crystallises in large plates, are formed.

Under the action of 30—40 per cent. sulphuric acid it is converted into *scutellarein*, $C_{15}H_{10}O_6$, which melts above 300°, dissolves in alkalis with a yellow colour, gives a reddish-brown tint with ferric chloride, an emerald-green colour with baryta water, and a yellowish-red precipitate with lead acetate. When fused with potash, scutellarein yields *p*-hydroxybenzoic acid and phloroglucinol (?). Scutellarin and scutellarein both appear to be flavone derivatives; the latter is probably represented by the formula



$$C_6H_3(OH)_2 \begin{cases} O{-}C\cdot OH \\ \quad\;\; \| \\ CO\cdot C\cdot C_6H_4\cdot OH \end{cases}$$

$[(OH)_4 = 2:5:7:4']$, and is isomeric with the substance [kampherol (?)] described by A. G. Perkin and Wilkinson (Proc., 1900, **16**, 182), from which *p*-hydroxybenzoic acid and phloroglucinol are obtained on fusion with potash. K. J. P. O.

Phoenicein, the Dye from Purple Wood (Copaifera Bracteata). By Estella Kleerekoper (*Chem. Centr.*, 1901, ii, 858; from *Ned. Tijd. Pharm.*, **13**, 245—255).—The bark parenchyma cells of *Copaifera bracteata* contain phoenin, $C_{14}H_{16}O_7$, the glucoside of the leuco-compound of phoenicein, in solution; it is found principally in the core-wood; when boiled with hydrochloric acid it gives a red coloration, the glucoside being probably decomposed and the leuco-compound oxidised. Phoenin crystallises from water in minute, colourless needles or rods, and on exposure to the air becomes slightly violet; at 100°, it loses 6 per cent. of water and decomposes, forming a dye. Its solution in alkalis has a pale brown colour, but quickly becomes darker and decomposes, the dye being then no longer precipitated by acids. Phoenicein, prepared by boiling phoenin with methyl alcohol and hydrochloric acid and treating with water, forms a red precipitate, which retains hydrochloric acid with great obstinacy. It is somewhat soluble in water containing a small quantity of hydrochloric acid, and with ammonia gives a violet-blue coloration. Purple wood yields about 2 per cent. of phoenicein. E. W. W.

Scatole-red and Similar Colouring Matters of Urine. By Karl Rössler (*Chem. Centr.*, 1901, ii, 861—862; from *Centr. inn. Med.*, **22**, 847—855).—When the indican test is applied to urine, especially when Obermeyer's method is employed, the liquid above the chloroform layer is often coloured in shades varying from brown to violet. As a rule, the dye is soluble in amyl alcohol, forming a brown solution. The same colouring matter may also be frequently obtained by treating the urine with fuming hydrochloric acid and extracting with amyl alcohol. Attempts to isolate indigo-red, urorosein, and scatole-red failed, however. By the action of hydrochloric acid on urine, neither indigo-red nor urorosein is formed, but the solubility of the dye and the fact that more is formed when scatole is introduced into the organism, render it probable that scatole-red is the colouring matter in this case. In order to detect scatole-red, 10 c.c. of urine are treated with an equal volume of fuming hydrochloric acid, and after remaining five minutes the mixture is shaken with amyl alcohol. If the extract, instead of showing a brownish-red colour, has a mixed colour with a tinge of blue, or if the urine is decomposed, a small quantity of lead acetate is added, and after removing indigo-red and indigo-blue from the filtrate by shaking with chloroform, the scatole-red is extracted by means of amyl alcohol. E. W. W.

Furfurandicarboxylic Acid. Its Preparation, Salts, and Esters. By P. A. Yoder and Bernhard Tollens (*Ber.*, 1901, **34**, 3446—3462).—Furfurandicarboxylic acid may be obtained in 24 per cent. yield by heating mucic acid with twice its weight of concentrated sulphuric acid for 40 minutes in a glycerol-bath kept at a temperature of 133—137°, and is purified by conversion into its barium salt. The following salts are described: *sodium*, $C_6H_2O_5Na_2,4H_2O$; *potassium*, with 1·5 or $2H_2O$; *strontium*, with $6H_2O$; *magnesium*, with $6H_2O$; *cadmium*, with $4·5H_2O$; *copper*, with 2·5 or $3H_2O$; *basic copper* salt, $C_6H_2O_5Cu,Cu(OH)_2,3H_2O$. The *ammonium* and *lead* salts are anhydrous. The normal esters have the following melting and boiling points:

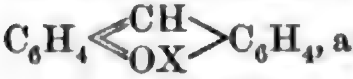
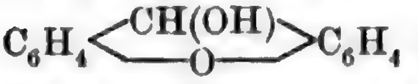
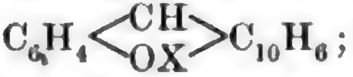
	M. p.	B. p.
Methyl	112°	154—156° under 15 mm. pressure
Ethyl	47	167—168 „ 16 „
n-Propyl	21—21·5	177—178 „ 15 „
iso-Propyl	42—42·5	156—159 „ 13 „
n-Butyl	37—38	186—190 „ 13 „
iso-Butyl	88	172—174 „ 13 „
iso-Amyl	37·5	207—211 „ 18 „

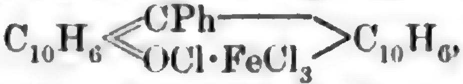
The authors cannot confirm Schmidt and Cobenzl's statement (Abstr., 1884, 1125) that potassium furfurandicarboxylate is formed when potassium mucate is heated. Furfurandicarboxylic acid and a number of its derivatives and allied substances have been treated with isatin and sulphuric acid, and the temperature at which a colour is produced noted. J. J. S.

Phenoxozone Derivatives. By HOMER W. HILLYER (*Amer. Chem. J.*, 1901, **26**, 361—372).—When dinitrophenoxozone, obtained by the action of picryl chloride on catechol (Abstr., 1900, i, 289), is reduced with tin and hydrochloric acid, *diaminophenoxozone*, $C_6H_4{:}O_2{:}C_6H_2(NH_2)_2$, is obtained, which crystallises in needles, melts and blackens at 198—200°, and acts both as a mono- and di-basic substance with chloroplatinic acid. Its *diacetyl* derivative crystallises in minute, lustrous scales and melts and darkens at 252·5—253°. The *benzoyl* derivative melts at 274—275°.

Dinitrophenoxozone dissolves in alcoholic sodium ethoxide to form a carmine-coloured solution, from which it is reprecipitated on addition of water. If sodium hydroxide is used instead of the ethoxide, *dinitrodihydroxyphenoxide*, $OH{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_2(NO_2)_2{\cdot}OH$, is produced, which melts at 153—153·5°, is slightly soluble in water, and yields *ammonium*, *silver*, and *mono-* and *di-sodium* salts; its *dimethyl ether* melts at 119—120°. On reduction with tin and hydrochloric acid, a substance is produced which furnishes a light violet hydrochloride.

When 3-nitrocatechol is treated with picryl chloride, a yellow, crystalline condensation product is obtained. Picryl chloride reacts with pyrogallol with formation of *dinitrohydroxyphenoxozone*, $OH{\cdot}C_6H_3{:}O_2{:}C_6H_2(NO_2)_2$, which crystallises from acetic acid in brown, transparent spikes, melts and decomposes at 258—258·5°, and is readily soluble in nitrobenzene, glacial acetic acid, or acetone, and fairly so in alcohol, phenol, or ethyl acetate, but only sparingly so in hot water. On reduction with tin and hydrochloric acid, a *base* is obtained which crystallises in needles, melts at 252—253°, and is soluble in alcohol or acetone. E. G.

Carboxonium and Carbothionium Salts. By ALFRED WERNER (*Ber.*, 1901, **34**, 3300—3311).—Xanthhydrol (Meyer and Saul, Abstr., 1893, i, 471) dissolves in acids to form xanthoxonium salts of the type  $C_6H_4<\begin{smallmatrix}CH\\OX\end{smallmatrix}>C_6H_4$, and in all probability is itself a ψ-xanthoxonium base,  $C_6H_4<\begin{smallmatrix}CH(OH)\\O\end{smallmatrix}>C_6H_4$ (compare Collie and Tickle, Trans., 1899, **75**, 710, and Kehrmann, Abstr., 1900, i, 61; 1901, i, 484); the simple salts are very soluble and cannot be isolated, but double salts, like the crystalline *ferrichloride*, $C_{13}H_9OCl_4Fe$, *perbromide*, $C_{13}H_9OBr_3$, *platinichloride*, and *mercurichloride* are readily obtained; the latter forms long, yellow, spear-like prisms. Pheno-α-naphthoxanthhydrol also yields salts of the type  $C_6H_4<\begin{smallmatrix}CH\\OX\end{smallmatrix}>C_{10}H_6$; the reddish-brown *ferrichloride*, $C_{17}H_{11}OCl_4Fe$, and the brown *perbromide* were prepared.

On oxidising benzylidene-β-dinaphthyloxide in acetic acid solution containing hydrochloric acid with manganese dioxide and adding ferric chloride, the *salt*,  $C_{10}H_6<\begin{smallmatrix}CPh\\OCl{\cdot}FeCl_3\end{smallmatrix}>C_{10}H_6$, separates and can be crystallised from glacial acetic acid in long, orange needles; on dissolving this in acetone containing water, colourless, concentric aggregates of flat needles separate, which melt at 248° and consist of the *anhydride* $\left(O{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}CPh\right)_2O$, of the ψ-base. This dissolves in acids, yielding salts, which, however, are best obtained by dissolving the anhydride in glacial acetic acid and adding the acid; the *perbromide*, $C_{27}H_{17}OBr_3$, forms lustrous, golden leaflets, which, on rubbing, change to a reddish-yellow powder. On warming the above-mentioned ferrichloride with absolute alcohol, the *ethoxide*, $C_{10}H_6{<}\begin{matrix}CPh(OEt)\\O\end{matrix}{>}C_{10}H_6$, of the ψ-base is obtained, which crystallises from benzene in white, acutely truncated prisms melting at 218—219°.

The reduction of xanthone, which, with zinc dust and hydrochloric acid yields dixanthylene (Gurgenjanz and Kostanecki, Abstr., 1896, i, 52), gives, with zinc and hydrobromic acid, *dixanthoxonium zincobromide*, $BrO{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C{\cdot}C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}OBr,ZnBr_2$; the *ferrichloride* obtained from this is beautifully crystalline. Dixanthylene itself can readily be converted into *dixanthoxonium nitrate*, $(C_{13}H_8O{\cdot}NO_3)_2$, by suspending it in benzene and saturating with nitrous fumes at 60—70°; the nitrate forms stout, brown crystals with a bluish lustre, and is converted by hydrobromic acid into the corresponding *bromide*, which readily dissolves in water and yields a black, additive compound with alcohol.

Pyrone, like dimethylpyrone, yields crystalline salts; the *platinichloride* forms large, flat, amber-yellow crystals. Fluorescein, rhodamine, rosamine, and pyronine dyes are probably oxonium salts.

Thioxanthone, on reduction with zinc and alcoholic sodium hydroxide, yields *thioxanthhydrol*, $C_6H_4{<}\begin{matrix}CH(OH)\\S\end{matrix}{>}C_6H_4$, a ψ-base which crystallises from light petroleum in needles, melts at 150°, and yields salts analogous to those of xanthhydrol; the *perbromide*, $C_6H_4{<}\begin{matrix}CH-\\SBr_3\end{matrix}{>}C_6H_4$, forms copper-red, lustrous leaflets. The chromophoric character of the thionium group is apparently greater than that of the oxonium radicle. W. A. D.

Amine derived from the supposed Dinaphthylene Glycol. By R. Fosse (*Compt. rend.*, 1901, **133**, 639—641. Compare this vol., i, 604, 643).—The author shows that the so-called bromide and amine prepared from the supposed dinaphthylene glycol by Rousseau (Abstr., 1884, i, 180) are in reality dinaphthoxanthone derivatives and respectively identical with bromodinaphthoxanthone and bisdinaphthoxanthoneamine obtained from dinaphthoxanthone (*loc. cit.*). K. J. P. O.

Hyoscine and Atroscine. By Oswald Hesse (*J. pr. Chem.*, 1901, [ii], **64**, 353—386).—A detailed description of the salts and derivatives of hyoscine and atroscine, which shows the correctness of the author's opinion (Abstr., 1897, i, 232, and 1900, i, 51) that optically active scopolamine (see Schmidt, Abstr., 1895, i, 158) is identical with hyoscine. Hyoscine dissolves in 9·5 parts of water at 15° and forms the following salts in addition to those previously described (*loc. cit.*, and also Abstr., 1896, i, 656); the *hydrochloride*, $C_{17}H_{21}O_{3}N,HCl$, crystallises from acetone and melts at 197°; the *hydrobromides* crystallise with $\frac{1}{2}H_2O$, with H_2O, and with $2H_2O$; the *hydriodide* crystallises from alcohol in compact prisms with H_2O and melts at 197° when anhydrous; the *salicylate* is a syrup and the *sulphate*, $(C_{17}H_{21}O_4N)_2,H_2SO_4,2H_2O$, crystallises in microscopic needles. The rotation of hyoscine has not yet been accurately determined; it seems, however, to be about $[\alpha]_D$ −33°. *Acetylhyoscine*, $C_{17}H_{20}O_4NAc$, obtained by the action of acetic anhydride on hyoscine hydrobromide, is a syrup, which, when hydrolysed with barium hydroxide, yields oscine, and atropic and acetic acids; it forms an *aurichloride*,

$$C_{17}H_{20}O_4NAc,HAuCl_4,$$

which crystallises in leaflets melting at 148° and a *hydrobromide* which is an amorphous powder with $[\alpha]_D$ −8·9°. Hyoscine methiodide melts at 208° [not at 215° as given by Schmidt for scopolamine methiodide (*loc. cit.*)] and has $[\alpha]_D$ −13·8°, the *methochloride* crystallises, with H_2O, in large, colourless prisms, melts, when anhydrous, at 189° and forms an amorphous *platinichloride* and an *aurichloride* melting at 143°, the *methobromide* is obtained in large, colourless crystals with H_2O and melts at 214° when anhydrous. Hyoscine ethiodide has the properties of scopolamine ethoxide (Schmidt, *loc. cit.*), the *ethobromide* and *ethochloride* are also described.

Atroscine dissolves in 37 parts of water at 18° and the melting points of its anhydrous hydrobromide and hydriodide are now given as 181° and 192° respectively. *Acetylatroscine*, $C_{17}H_{20}O_4NAc$, is a colourless syrup soluble in hydrochloric acid and precipitated by alkalis, is inactive, and forms an *aurichloride*, which begins to sinter at 120° and melts at 140°, and a *platinichloride*, which is obtained with $2H_2O$, as an amorphous precipitate melting at about 165°. The *methiodide* crystallises, with H_2O, in colourless, lustrous prisms and, when anhydrous, melts at 202°, the *methobromide* crystallises, with H_2O, in compact prisms and melts at 207° when anhydrous, the *methochloride* crystallises, with H_2O, in lustrous prisms, and forms an *aurichloride* melting at 146°; these, when treated with moist silver oxide, give a solution of the *methohydroxide*, which is strongly alkaline. The *ethiodide* crystallises in octahedra, melts at 170°, and forms an *aurichloride* melting at 124°. Atroscine is best obtained from hyoscine hydrobromide by treatment with sodium hydroxide.

The paper concludes with an account of the pharmaceutical uses of hyoscine, atroscine, and "scopolamine." R. H. P.

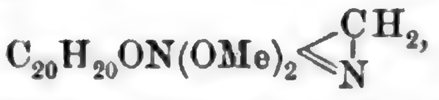
Diclytra Spectabilis. By JOHANNES GADAMER (*Chem. Centr.*, 1901, ii, 814; from *Apoth. Zeit.*, 1901, **16**, 621. Compare Battandier, *Compt. rend.*, 1892, **114**, 1122).—Protopine (macleyine, fumarine), $C_{20}H_{19}O_5N$, extracted from the roots of *Diclytra spectabilis* by means of alcohol containing acetic acid, separates from chloroform and ethyl acetate in dull, crystalline aggregates, melts at 201—202°, and forms an anhydrous hydrochloride (compare Hopfgartner, Abstr., 1898, i, 606). Protopine prepared from *Chelidonium majus* also melts at 201—202°. The roots of *Corydalis cava* do not appear to contain protopine. E. W. W.

Cinchotinesulphonic Acid. By Theodor Schmid (*Monatsh.*, 1901, **22**, 803—812).—When heated with potassium hydroxide at 100°, cinchotinesulphonic acid is not changed; when heated at 184° with potassium hydroxide in the presence of amyl alcohol, it yields a *base*, $C_{19}H_{20}N_2$, the *picrate* of which melts at 183°. At 140°, the sulphonic acid gives *hydroxycinchotine*, $C_{19}H_{24}O_2N_2$; the *picrate* melts at 156°. On oxidation of cinchotinesulphonic acid or hydroxycinchotine by chromic acid, cinchonic acid is formed, a fact which shows that the sulphonic acid group is probably in the so-called second half of the cinchotine molecule.

Hydroquininesulphonic acid is not attacked by potassium hydroxide at 100°, but by hydrochloric acid is hydrolysed to hydroquinine and sulphuric acid. K. J. P. O.

Electrolytic Reduction of Strychnine and of Brucine. By Julius Tafel and Kurt Naumann (*Ber.*, 1901, **34**, 3291—3299).—The electrolytic reduction of strychnine in sulphuric acid solution using lead electrodes and a closed vessel (compare Abstr., 1898, i, 703; 1900, ii, 588) gives tetrahydrostrychnine almost entirely (70 per cent.) at a temperature of −2° to 1°; at 35—43°, nearly equal quantities of tetrahydrostrychnine and strychnidine are obtained, the latter being produced from the former by the separation of water brought about by the sulphuric acid at the higher temperature.

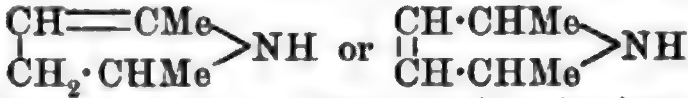
A similar reduction of brucine at 15° gave principally a *tetrahydrobrucine*, $OH{\cdot}CH_2{\cdot}C_{20}H_{20}ON(OMe)_2{:}NH$, which crystallises from methyl alcohol in colourless prisms, begins to decompose at 185°, and ultimately melts at 200—201° to a yellow liquid; the reduction at temperatures above 15° is more rapid, but a crystalline product cannot then be isolated, substances extremely sensitive to the action of the air being formed. *Tetrahydrobrucine hydrochloride*, $C_{23}H_{30}O_4N_2,HCl$, crystallises from alcohol in thin, colourless leaflets; the *platinichloride*, *mercurichloride* and *picrate* are amorphous; the *dihydrochloride*, $C_{23}H_{30}O_4N_2,2HCl$, separates from hot alcohol in colourless crystals which rapidly become greenish in the air. With nitrous acid, tetrahydrobrucine does not yield a nitrosoamine.

Brucidine, 
$C_{20}H_{20}ON(OMe)_2{<}\begin{matrix}CH_2,\\ |\\ N\end{matrix}$ which is not formed during the electrolytic reduction of brucine, is obtained by heating tetrahydrobrucine at 220° in a stream of hydrogen for 40 minutes; it crystallises from ethyl acetate in nodules of silky needles, becomes brownish at 195° and melts at 198°. The *hydrochloride* is similar to that of tetrahydrobrucine.

Unlike strychnidine and tetrahydrostrychnine, which can be readily distinguished from one another by colour reactions in acid solution with ferric chloride, chromic acid, and nitrous acid, brucidine and tetrahydrobrucine give very similar indications with these reagents.

The electrolytic reduction of quinine, cinchonine, and cinchonidine, did not give crystalline products. W. A. D.

Transformation of Pyrroles into Pyrrolines. By Ludwig Knorr and Paul Rabe [and, in part, H. Bufleb and C. Jakobi] (*Ber.*, 1901, **34**, 3491—3502).—Better yields of pyrroline are obtained by reducing pyrroles with zinc and hydrochloric acid than by using zinc and acetic acid, as recommended by Ciamician and Dennstedt (Abstr., 1883, 82).

2 : 5-*Dimethylpyrroline*,  $\begin{matrix}CH{=\!=}CMe\\ |\\ CH_2\cdot CHMe\end{matrix}\!>\!NH$ or $\begin{matrix}CH\cdot CHMe\\ \|\\ CH\cdot CHMe\end{matrix}\!>\!NH$, obtained from 2 : 5-dimethylpyrrole, boils at 106° (corr.) under 736 mm. pressure, and has a sp. gr. 0·8369 at 20°/4°, and n_D 1·4401 at 20°; the *platinichloride* forms orange-coloured prisms or rhombs, and melts and decomposes at 198°; the *aurichloride* melts and sinters at 68—69°, and decomposes at 150°; the *picrate* melts at 105°, and the characteristic *picrolonate* at 130° with decomposition.

2 : 4-*Dimethylpyrroline* boils at 121° (corr.) under 752 mm. pressure, and has a sp. gr. 0·8554 at 20°/4°, and n_D 1·4493 at 20°. The *platinichloride* (needles) melts at 185°, the *picrate* (prisms) at 102—104°, and the *picrolonate* at 225°; 1 : 2 : 4-*trimethylpyrroline* is a highly deliquescent, crystalline mass, but gives an *aurichloride* crystallising in orange-coloured needles, and melting at 251°.

1 : 2 : 5-*Trimethylpyrroline* boils between 105° and 120°; the fraction between 105° and 110° has a sp. gr. 0·8138 at 20°/4°, and n_D 1·4334 at 20°; that boiling at 110—115° (largest fraction) has a sp. gr. 0·8131 at 20°/4°, and n_D 1·4365 at 20°, and that boiling at 115—120° has a sp. gr. 0·8206 at 20°/4°, and n_D 1·4422 at 20°. The three fractions have a practically identical composition and yield identical salts; the *platinichloride* (brown, irregular plates) melts at 150°; the *aurichloride* (rosettes of plates) melts and decomposes at 115°, the *picrate* (needles) at 195—205°, and the *picrolonate* (prisms) at 180—190°. The *methiodide* forms white scales, is very hygroscopic, and melts at about 310°.

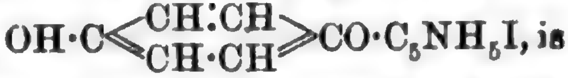
Pyrroline (compare Ciamician and Dennstedt, *loc. cit.*) boils at 90° (corr.) under 748 mm. pressure, and has a sp. gr. 0·9097 at 20°/4°, and n_D 1·4664 at 20°; the platinichloride melts and decomposes at 182°, and the *picrolonate* forms yellow, rhombic plates, darkens at 235°, and melts and decomposes at 260°.

The foregoing pyrrolines are reduced by heating with hydriodic acid and phosphorus to pyrrolidines, but the yield is generally poor.

2 : 4-*Dimethylpyrrolidine* boils at 115—117° (corr.) under 753 mm. pressure, and has a sp. gr. 0·8297 at 20°/4°, and n_D 1·4325 at 20°; the *platinichloride* (needles) melts at about 210°, the *picrate* at 116—117°, and the *picrolonate* at 227°.

1 : 2 : 5-*Trimethylpyrrolidine picrate* melts at 163°, the *picrolonate* at 193°, and the *methiodide* at 310° (compare Tafel and Neugebauer, Abstr., 1890, 1000, and Merling, Abstr., 1891, 1506). W. A. D.

***iso*Coniine.** By Albert Ladenburg (*Ber.*, 1901, **34**, 3416).—Polemical (compare Abstr., 1897, i, 173). J. J. S.

Action of Iodine on a Pyridine Solution of Quinol. By Giovanni Ortoleva and G. di Stefano (*Gazzetta*, 1901, **31**, ii, 256—265. Compare Abstr., 1900, i, 558 and 592).—By the action of iodine on a solution of quinol in a mixture of alcohol and pyridine, or by the interaction of aqueous quinol and excess of pyridine hydriodide, or by the addition of concentrated hydriodic acid to a pyridine solution of quinol, an *additive* compound,  $OH\cdot C\langle\begin{smallmatrix}CH:CH\\CH\cdot CH\end{smallmatrix}\rangle CO\cdot C_5NH_5I$, is obtained; it crystallises from water in long, stout needles, which blacken at 240° and melt at 254°. It dissolves in alcohol, and silver nitrate precipitates the iodine quantitatively from its aqueous solution. Alcoholic potassium hydroxide dissolves it, giving a violet colour, whilst its solutions in aqueous alkali hydroxides and carbonates are deep red and, when acidified with sulphurous acid, yield the unaltered compound. Its *acetyl* derivative, $C_{11}H_9O_2NIAc$, crystallises from water in large, yellowish plates containing $1H_2O$, and from chloroform in long, flat, faintly yellow needles which melt at 165—168°, and are soluble in acetic acid.

The corresponding *chloro*-compound, $C_6H_4O_2,C_5NH_5,HCl$, obtained by the action of concentrated hydrochloric acid on a pyridine solution of quinol, or in quantitative yield by the action of hydrochloric acid on the iodo-compound, crystallises from water in thin needles melting at 223—225°, and dissolving in alcohol.

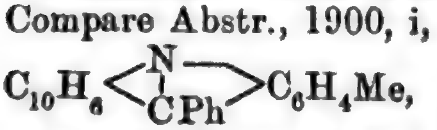
The *bromo*-compound, $C_6H_4O_2,C_5NH_5,HBr$, prepared in a similar manner, forms brownish-yellow needles melting at 230°, and has properties analogous to those of the other two compounds.

T. H. P.

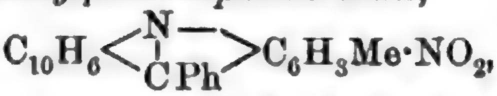
Action of Pyridine Bases on Tetrahalogenated Quinones. Quinol Derivatives. By Henri Imbert (*Compt. rend.*, 1901, **133**, 633—634. Compare Abstr., 1901, 651, 652).—Pyridyldichlorohydroxyquinone, $C_5NH_4\cdot C_6Cl_2O_2(OH)$ (*loc. cit.*), is converted by a boiling concentrated aqueous solution of sulphur dioxide into *pyridylchlorohydroxyquinolsulphonic acid*, $C_5NH_4\cdot C_6Cl(OH)_3\cdot SO_3H$, which crystallises from water in pearly needles; its aqueous solution reduces Fehling's solution and gives a dark red coloration with ferric chloride, a blue coloration with ferrous sulphate, and a bright red coloration with platinic salts. The alkaline solutions rapidly darken on exposure to air.

The mother liquor, from which the compound just mentioned has separated, deposits, on addition of sodium acetate, *pyridyldichlorohydroxyquinol sulphate*, $C_5NH_4\cdot C_6Cl_2(OH)_3,H_2SO_4$; this substance forms colourless crystals, which rapidly become red in contact with air, or on exposure to light. The aqueous solution becomes red on treatment with oxidising agents and reduces Fehling's solution.

K. J. P. O.

Naphthacridine Derivatives. Fritz Ullmann (D.R.-P. 117472. Compare Abstr., 1900, i, 360).—5-*Phenyl-3-methylphenonaphthacridine*,  $C_{10}H_6\langle\begin{smallmatrix}N\\|\\CPh\end{smallmatrix}\rangle C_6H_4Me$, produced by condensing benzylidene-*p*-toluidine with β-naphthol, is a yellow, crystalline powder melting at 213°; it has slightly basic properties and forms a yellow nitrate and sulphate.

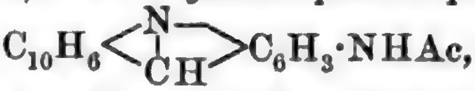
5-m-*Nitrophenyl-3-methylphenonaphthacridine*,



$$C_{10}H_6\left\langle\begin{matrix}N\text{—}\\ | \\ CPh\end{matrix}\right\rangle C_6H_3Me\cdot NO_2,$$

prepared in a similar manner from *m*-nitrobenzylidene-*p*-toluidine, separates from benzene or glacial acetic acid in pale yellow crystals and melts at 273°. G. T. M.

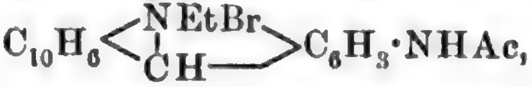
Preparation of Acridinium Colouring Matters. Fritz Ullmann (D.R.-P. 118439. Compare Abstr., 1900, i, 361, 689, and preceding abstract).—3-*Acetylaminophenonaphthacridine*,



$$C_{10}H_6\left\langle\begin{matrix}N\text{—}\\ | \\ CH\end{matrix}\right\rangle C_6H_3\cdot NHAc,$$

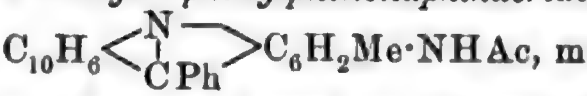
produced by heating acetyl-*p*-phenylenediamine, trioxymethylene and β-naphthol at 180°, crystallises from alcohol in yellow, felted needles and melts at 255°.

Ethyl-3-acetylaminophenonaphthacridinium bromide,

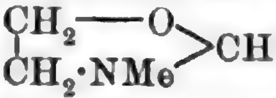


$$C_{10}H_6\left\langle\begin{matrix}NEtBr\\ | \\ CH\text{—}\end{matrix}\right\rangle C_6H_3\cdot NHAc,$$

prepared by heating the preceding substance with ethyl bromide in chloroform or benzene solution at 150°, yields a yellow solution and on hydrolysis furnishes a base forming red, soluble salts. The salts of the base dye cotton mordanted with tannin in reddish shades, whilst those of the acetyl derivative give orange-yellow tints. These quaternary salts are not affected by ammonia or the alkali carbonates; alkali hydroxides, however, decompose them, setting free the colour base as a red precipitate.

2-*Amino-3-methyl-5-phenylphenonaphthacridine* yields an *acetyl derivative*,  $C_{10}H_6\left\langle\begin{matrix}N\text{—}\\ | \\ CPh\end{matrix}\right\rangle C_6H_2Me\cdot NHAc$, melting at 255—256°, the latter compound, when heated at 160—170° with ethyl bromide in chloroform solution, gives rise to a quaternary *ethobromide*, which, on hydrolysis, furnishes the corresponding *amino-ethobromide*. The dyeing properties of these quaternary salts are similar to those of the analogues just described. G. T. M.

Sythesis of Oxazolidines by the Action of Aldehydes on Hydramines. By Ludwig Knorr and Hermann Matthes (*Ber.*, 1901, 34, 3484—3489).—The following compounds were prepared by boiling equivalent quantities of the hydramine, $OH\cdot CH_2\cdot CH_2\cdot NHR$, and aldehyde in ethereal solution for several hours in presence of potassium carbonate; they are easily hydrolysed by aqueous acids and alkalis, and hence the only salts readily obtainable are the picrates.

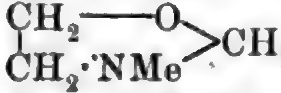
2-*Phenyl-3-methyloxazolidine*,  $\begin{matrix}CH_2\text{——}O\\ | \\ CH_2\cdot NMe\end{matrix}\!\!>CHPh$, obtained from benzaldehyde and methylhydroxyethylamine, boils at 240° under 746 mm., and yields a *picrate* which melts indefinitely at 110°, and is converted by recrystallisation into methylhydroxyethylamine picrate. On oxidation with chromic acid, it gives sarcosine and benzoic acid.

2-*Phenyloxazolidine*, obtained from benzaldehyde and hydroxyethylamine, boils at 284° under 748 mm. pressure.

2-*Phenyl*-3-*isobutyloxazolidine* boils at 266—268° under 754 mm. pressure, the *picrate* is yellow and melts at about 110°.

2 : 3-*Dimethyloxazolidine*, obtained from acetaldehyde and methylhydroxyethylamine, boils at 109° under 758 mm. pressure and yields a *picrate* melting indefinitely at 75°; when hydroxyethylamine is used, 2-*methyloxazolidine* is obtained, which boils at 140—142° under 748 mm. pressure and gives a *picrate* melting at about 75°.

3-*Methyloxazolidine*,

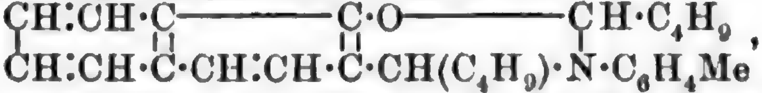


$\begin{array}{l}CH_2\text{——}O\\ |\\ CH_2\cdot NMe\end{array}\!\!>CH_2$

, is obtained only in poor yield from formaldehyde and methylhydroxyethylamine and boils at 100° under 735 mm. pressure; the *picrate* melts at 152°. W. A. D.

Synthesis of α-Naphtho*iso*oxazine Derivatives. By Mario Betti (*Gazzetta*, 1901, **31**, ii, 209—215. Compare Abstr., 1901, i, 753).—The 2 : 3 : 4-triphenyl-1 : 3-α-naphtho*iso*oxazine, prepared by the interaction of benzylidene-α-naphthol and benzaldehyde (*loc. cit.*), can be obtained directly from α-naphthol, benzaldehyde, and aniline; it crystallises from benzene in small scales, which turn yellow at 150° and melt at 158—160°. The melting point varies very considerably with the solvent from which crystallisation takes place; thus, by heating with acetic anhydride, no acetyl compound is obtained, but the original substance is recovered, the melting point being raised to 195—197°.

2 : 4-*Dibutyl*-3-*tolyl*-α-*naphthoisooxazine*,



$$\begin{array}{l}CH{:}CH\cdot C\text{————}C\cdot O\text{————}CH\cdot C_4H_9\\ |\qquad\quad\ \ \|\qquad\quad\ \|\qquad\qquad\quad |\\ CH{:}CH\cdot C\cdot CH{:}CH\cdot C\cdot CH(C_4H_9)\cdot N\cdot C_6H_4Me\end{array},$$

prepared from α-naphthol, *p*-toluidine, and valeraldehyde, separates from alcohol in shining, white needles melting at 191°. With cold ferric chloride it gives no colour, but on boiling, an intense carmine coloration is produced which does not disappear on cooling. T. H. P.

Preparation of Alkylhydrazines. By Robert Stollé (*Ber.*, 1901, **34**, 3268—3269. Compare Abstr., 1896, i, 407; 1898, i, 231).—The monoalkylhydrazines are readily obtained by heating hydrazine with an aqueous solution of the corresponding alkyl sulphate; the product is freed from unaltered base by treating the mixture with benzaldehyde, and isolated in the form of its benzoyl derivative by the aid of the Schotten-Baumann reaction. The dibenzoyl derivatives of ethyl- and propyl-hydrazines may be prepared in this manner. *Dibenzoylisobutylhydrazine*, $N_2HBz_2\cdot C_4H_9$, and *dibenzoylamylhydrazine*, $N_2HBz_2\cdot C_5H_{11}$ (from *iso*butylcarbinol) melt respectively at 167° and 133°. These dibenzoyl compounds dissolve in dilute sodium hydroxide solution and do not reduce ammoniacal silver nitrate or Fehling's solution even on boiling. G. T. M.

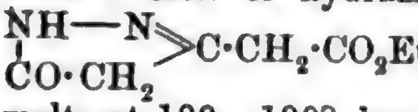
Hydrazide and Azoimide of Phenylpropionic Acid. By Heinrich Jordan (*J. pr. Chem.*, 1901, [ii], **64**, 297—313).—*Phenylpropionylhydrazide* is obtained in quantitative yield by treament of ethyl phenylpropionate with hydrazine hydrate; it crystallises from water in long, prismatic needles melts at 103°, and yields a *hydrochloride*, which forms lustrous, long, prismatic needles and gives condensation *compounds* with benzaldehyde, salicylaldehyde, ethyl acetoacetate and acetone; these are colourless, crystalline substances melting respectively at 132·5°, 148·5°, 95°, and 93°. When treated with iodine in alcoholic solution, the hydrazide yields *s-diphenylpropionylhydrazine*, which crystallises in prismatic needles melting at 208°; this, when treated with nitrous acid, gives *phenylpropionylazide*, which is obtained as a light powder with a penetrating odour.

The azoimide, when boiled with ethyl alcohol, yields *ethyl β-phenylethylcarbamate*, which crystallises in small laminæ, melts at 33·5°, and, when treated with water, gives diphenylethylcarbamide (m. p. 138·5°). The carbamate or the carbamide, when hydrolysed, yields β-phenylethylamine. The *hydrobromide* of the amine, which melts and decomposes at 257—259°, and *compounds* of the amine with mercuric chloride (m. p. 188°) and cadmium iodide (m. p. 102—103°) are described. The action of bromine on the azoimide was investigated, but only resulted in the formation of the hydrobromide of the amine. R. H. P.

Hydrazide and Azoimide of Phenylacetic Acid. By ERNST BOETZELEN (*J. pr. Chem.*, 1901, [ii], **64**, 314—323).—The following new compounds, obtained from phenylacetic acid by methods analogous to those described in the preceding abstract, have been prepared. *Phenylacetylhydrazide* forms long, slender needles melting at 116°; its *hydrochloride* crystallises in silky needles melting and decomposing at 215°. *Phenylacetylmethylenehydrazide* melts at about 64°. *Benzylidenephenylacetylhydrazide* forms prisms melting at 154°. *Salicylidenephenylacetylhydrazide* crystallises in broad prisms melting at 188°. The *phenylacetylhydrazide* of *ethyl acetoacetate* forms prisms melting at 105°. *Phenylacetylazoimide* forms a colourless, mobile oil with a penetrating odour, and has the properties characteristic of azoimides. The action of bromine on the azoimide yielded a colourless, crystalline *substance* melting at 121°. Ethyl benzylcarbamate and dibenzylcarbamide are easily obtained from the azoimide. R. H. P.

Hydrazide of *m*-Chlorobenzoic Acid. By HANS FOERSTER (*J. pr. Chem.*, 1901, [ii], **64**, 324—333).—Researches with *m*-chlorobenzoic acid analogous to those described in the two preceding abstracts. *m-Chlorobenzoylhydrazide* crystallises in long needles melting at 158°, and its *hydrochloride* in iridescent laminæ decomposing at 250°. The condensation *compounds* of the hydrazide, with benzaldehyde, *m*-nitrobenzaldehyde, cinnamaldehyde, and acetone, are all crystalline substances, of which those from benzaldehyde and acetone melt respectively at 118° and 97°. s-m-*Chlorobenzoylhydrazine* crystallises in aggregates of small needles and melts at 264°. The *azoimide* is a colourless oil with a very penetrating odour, and easily decomposes with alcohol and water, forming ethyl *m*-chlorophenylcarbamate and *m*-dichlorodiphenylcarbamide respectively. R. H. P.

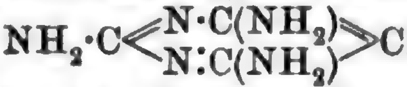
Pyrazolone-3-acetic Acid. By AUGUST KUFFERATH (*J. pr. Chem.*, 1901, [ii], 334—349).—Ethyl acetonedicarboxylate, when treated

with 1 mol. of hydrazine hydrate, yields *ethyl pyrazolone-3-acetate*,

$\begin{matrix}NH—N\\ |\\ CO\cdot CH_2\end{matrix}\!\!>C\cdot CH_2\cdot CO_2Et$, which crystallises from water in laminæ, melts at 189—190°, has physiological actions similar to those of antipyrine, and forms an *acetyl* derivative, which is a microcrystalline powder melting at 116—117°. When treated with nitrous acid, it yields *ethyl* 4-iso*nitrosopyrazolone-3-acetate*, which crystallises in lustrous, golden-yellow leaflets, melts at 114—115·5°, and forms an unstable, red *silver* salt. The silver salt, when treated with ethyl iodide, forms the corresponding *ethoxy*-derivative, which crystallises in small, yellow plates and melts at 116—117°. *Ethyl* 4-p-*azotoluene-pyrazolone-3-acetate*, obtained by the action of *p*-diazotoluene sulphate on the pyrazolone acetate, crystallises in dark-yellow needles and melts at 172—173°.

Pyrazolone-3-acetylhydrazide, obtained when ethyl acetonedicarboxylate is treated with an excess of hydrazine hydrate, is a microcrystalline powder, which melts and decomposes at 180°, and forms crystalline condensation *compounds* with benzaldehyde, salicylaldehyde, *m*-nitrobenzaldehyde, and cinnamaldehyde, melting and decomposing at 190°, above 200°, above 145°, and above 145° respectively. The *dihydrochloride* is a stable, crystalline powder which melts at 104—105°; when treated with sodium nitrite, it yields 4-iso*nitrosopyrazolone-3-acetylazoimide*, which forms yellow crystals melting at 97—98°. The azoimide, when treated with aniline, yields 4-iso*nitrosopyrazolone-3-acetanilide*, which is a brown powder melting and decomposing at above 165°.

R. H. P.

Amino-derivatives of Pyrimidine. By SIEGMUND GABRIEL (*Ber.*, 1901, **34**, 3362—3366. Compare Abstr., 1901, i, 168).—2 : 4 : 6-Trichloropyrimidine reacts with alcoholic ammonia under different conditions, yielding dichloroamino-, chlorodiamino-, and triamino-pyrimidines.

2 : 4 : 6-*Triaminopyrimidine*,

$NH_2\cdot C\!\!<\!\!\begin{matrix}N\cdot C(NH_2)\\ N:C(NH_2)\end{matrix}\!\!>CH$, is prepared by heating trichloropyrimidine or dichloroaminopyrimidine with alcoholic ammonia at 215°, and crystallises in short, colourless prisms, which sinter at 242° and melt at 245—246°. It is readily soluble in water, to which it imparts an alkaline reaction. The *nitrate* is sparingly soluble, the *hydrochloride*, $C_4H_7N_5,2HCl$, crystallises in compact prisms or rhombohedral forms, the *platinichloride*,

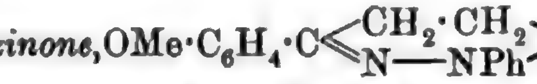
$$(C_4H_7N_5)_2,H_2PtCl_6,H_2O,$$

forms matted, lemon-yellow needles, and the *picrate* crystallises in long needles. The base is converted by fuming nitric acid and sulphuric acid into 5-*nitro*-2:4:6-*triaminopyrimidine*, $NO_2\cdot C_4N_2(NH_2)_3$, which crystallises in almost colourless, microscopic needles. The *hydrochloride* is decomposed by water, whilst the *platinichloride*, *aurichloride*, *picrate*, and *dichromate* are all crystalline. This compound is converted by reduction into *tetraminopyrimidine*, $C_4N_2(NH_2)_4$, which crystallises in flat, orange-yellow, pointed prisms, and decomposes when heated without showing a definite melting point. It is very soluble in water, forming a strongly alkaline solution. The *hydrochloride*, $C_4H_8N_6,3HCl$, forms oblong, readily soluble tablets; the *picrate* is microcrystalline, and the *platinichloride* forms stellate, yellow needles, but rapidly decomposes. A. H.

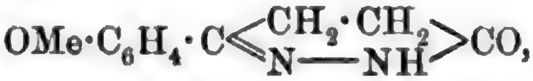
Transformation of Dimethylketazine into 3 : 5 : 5-Trimethylpyrazoline. By Karl Wilhelm Frey and Robert Hofmann (*Monatsh.*, 1901, **22**, 760—776. Compare Curtius and Försterling, Abstr., 1894, i, 348).—The transformation of dimethylketazine into 3 : 5 : 5-trimethylpyrazoline is not only effected by maleic acid (*loc. cit.*), but also by oxalic, succinic, tartaric, acetic, boric, metaphosphoric, and orthophosphoric acids, when these acids are either free from water or in solution in non-ionising solvents. Aqueous solutions of acids decompose, but do not transform, the ketazine. Aqueous tartaric acid partially decomposes the ketazine, but also effects some transformation. A solution of hydrogen chloride in toluene does not decompose, but transforms, the ketazine.

K. J. P. O.

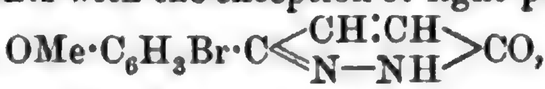
Pyridazines. By Otto Poppenberg (*Ber.*, 1901, **34**, 3257—3267. Compare Gabriel and Colman, Abstr., 1899, i, 390).—*Anisoylpropionic acid*, $OMe{\cdot}C_6H_4{\cdot}CO(CH_2)_2{\cdot}CO_2H$, resulting from the condensation of anisole and succinic anhydride in the presence of aluminium chloride, crystallises from water or the ordinary organic solvents in rhombic plates melting at 140—141°; it dissolves in concentrated solutions of the mineral acids to a deep red solution, the coloration being destroyed by dilution with water. The *silver* salt rapidly darkens on exposure to light.



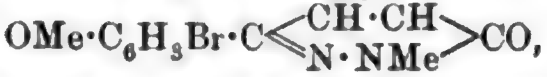
Anisylphenylpyridazinone, $OMe{\cdot}C_6H_4{\cdot}C{<}\begin{matrix}CH_2{\cdot}CH_2\\ N{-\!-}NPh\end{matrix}{>}CO$, produced by the action of phenylhydrazine on the alkali salts of the preceding acid, crystallises from alcohol in pale yellow, hexagonal pyramids and melts at 105°; it is insoluble in water, but readily soluble in the alcohols, ethyl acetate, or glacial acetic acid, whilst it dissolves only sparingly in ether, light petroleum, or chloroform.



Anisylpyridazinone, $OMe{\cdot}C_6H_4{\cdot}C{<}\begin{matrix}CH_2{\cdot}CH_2\\ N{-\!-}NH\end{matrix}{>}CO$, prepared by condensing anisoylpropionic acid with hydrazine hydrate in *N*-potassium hydroxide solution at the temperature of the water-bath, forms colourless, four-sided leaflets melting at 147—148°; it is soluble in hot water or the ordinary organic solvents with the exception of light petroleum.



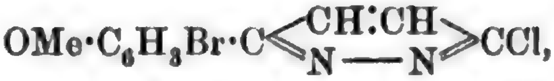
3-*Bromoanisylpyridazone*, $OMe{\cdot}C_6H_3Br{\cdot}C{<}\begin{matrix}CH{:}CH\\ N{-}NH\end{matrix}{>}CO$, obtained by the action of bromine (2 mols.) on the preceding compound, is a white, crystalline product melting at 263°; it is insoluble in the ordinary solvents, but dissolves, however, in solutions of the alkali hydroxides and also in glacial acetic acid. When heated with methyl iodide and sodium methoxide dissolved in methyl alcohol, the preceding pyridazone yields 3-*bromoanisyl*-1-*methylpyridazone*,



$$OMe{\cdot}C_6H_3Br{\cdot}C{<}\begin{matrix}CH{\cdot}CH\\ N{\cdot}NMe\end{matrix}{>}CO,$$

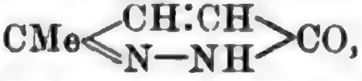
this substance separating in white needles melting at 153°; the corresponding *ethyl* derivative melts at 140°.

p-*Hydroxyphenylpyridazone*, $\mathrm{OH{\cdot}C_6H_4{\cdot}C}\Big<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{N-NH}\end{matrix}\Big>\mathrm{CO}$, resulting from the reduction of 3-bromoanisylpyridazone with red phosphorus and hydriodic acid, forms white crystals melting at above 290°; it dissolves in glacial acetic acid and in solutions of the alkali hydroxides. The *benzoyl* derivative, $C_{10}H_7O_2N_2\cdot COPh$, crystallises from alcohol in reddish leaflets melting at 254°.

3-*Bromoanisyl*-6-*chloropyridazine*,  $\mathrm{OMe{\cdot}C_6H_3Br{\cdot}C}\Big<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{N \longrightarrow N}\end{matrix}\Big>\mathrm{CCl}$, produced by the action of phosphorus oxychloride on bromoanisylpyridazone, crystallises from alcohol in pale yellow needles melting at 191°; when heated with sodium methoxide, it yields 3-*bromoanisyl*-6-*methoxypyridazine* melting at 137°, and with sodium ethoxide the corresponding *ethoxy*-compound melting at 114°. These pyridazine derivatives are all slightly basic; the chloro-compound dissolves in concentrated hydrochloric acid, but is reprecipitated by water; the methoxy- and ethoxy-bases yield *picrates* melting respectively at 146° and 154°. The chloro-base, on reduction, furnishes *p*-hydroxyphenylpyridazine (m. p. 227°; compare Gabriel and Colman, *loc. cit.*); the benzoyl derivative of this product forms needles melting at 179—180°, whilst its *nitro*-compound, $OH\cdot C_6H_3(NO_2)\cdot C_4H_3N_2$, melts somewhat indefinitely at 205° and is probably a mixture of isomerides. An *aminohydroxyphenylpyridazine* melting at 176° is obtained on reducing the nitration product with red phosphorus and hydriodic acid.

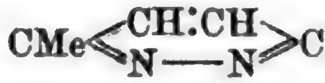
3-*Bromoanisyl*-6-*iodopyridazine*, obtained as an intermediate product in the formation of *p*-hydroxyphenylpyridazine, gives rise to 3-bromoanisyl-6-methoxypyridazine. Hydroxyphenylpyridazine could not be converted into a methoxy-base, but phenylpyridazine, when treated with methyl iodide, yields the *methiodide*, $C_4H_3N_2Ph\cdot MeI$, crystallising in yellow needles and melting at 179—180°.

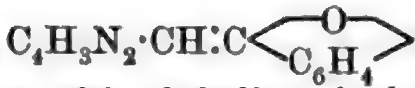
Methylpyridazinone is prepared in theoretical yield by evaporating to dryness an aqueous solution of lævulic acid, hydrazine sulphate, and alkali hydroxide and extracting the residue with alcohol.

3-*Methylpyridazone*,  $\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{N-NH}\end{matrix}\Big>\mathrm{CO}$, results from the action of bromine on the preceding compound in glacial acetic acid solution and crystallises from water in prisms melting at 143°.

1 : 3-*Dimethylpyridazone*, $\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{N{\cdot}NMe}\end{matrix}\Big>\mathrm{CO}$, obtained by methylating 3-methylpyridazone with methyl iodide and sodium methoxide, crystallises in colourless leaflets, boils at 224°, and melts at 38—39°. The corresponding *ethyl* derivative, $C_4H_2ON_2MeEt$, boils at 229—231° and is oily at the ordinary temperature.

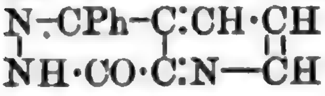
6-*Chloro*-3-*methylpyridazine*, $\mathrm{CMe}\Big<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{N \longrightarrow N}\end{matrix}\Big>\mathrm{CCl}$, produced by treating 3-methylpyridazone with phosphorus oxychloride on the water-bath, crystallises in snow-white needles and melts at 59°. The chlorine atom in this compound is readily replaced by an alkoxyl group, 3-*methyl*-6-*methoxypyridazine* being formed by the action of sodium methoxide; this product is an oily base boiling at 212—215°; the corresponding *ethoxy*-compound boils at 229—231°.

3-Methylpyridazine,  $\mathrm{CMe}<\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{N{—}N}\end{matrix}>\mathrm{CH}$, results from the reduction of 6-chloro-3-methylpyridazine with red phosphorus and hydriodic acid; it is an oil boiling at 214·5° under 760·5 mm. pressure and has a sp. gr. 1·0486 at 26°. The base yields well-crystallised, double salts with palladium, auric, platinic, and mercuric chlorides; the *picrate* crystallises in aggregates of needles and melts at 143—144°. 3-Methylpyridazine is miscible with water, yielding a neutral solution; it is slightly volatile in steam and readily dissolves in the ordinary organic solvents.

Methylpyridazinephthalone,  $\mathrm{C_4H_3N_2{\cdot}CH{:}C}<\begin{matrix}\mathrm{O}\\ \mathrm{C_6H_4}\end{matrix}>\mathrm{CO}$, prepared by condensing 3-methylpyridazine with phthalic anhydride at 210°, crystallises from glacial acetic acid in dark yellow needles and melts at 278°.

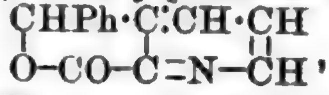
Cinnamenylpyridazine, produced by condensing 3-methylpyridazine with benzaldehyde, is isolated in the form of its *hydrochloride*, $\mathrm{CHPh{:}CH{\cdot}C_4H_3N_2,HCl}$, the yield of this product being, however, somewhat poor. The corresponding *platinichloride* decomposes on heating, whilst the *picrate*, $\mathrm{C_{12}H_{10}N_2,C_6H_3O_7N_3,2H_2O}$, melts at 199—213°.

G. T. M.

β-Benzoylpicolinic Acid. By BERTHOLD JEITELES (*Monatsh.*, 1901, **22**, 843—848. Compare Abstr., 1897, i, 97).—*3-Phenylquinolineazone*,  $\begin{matrix}\mathrm{N{-}CPh{-}C{:}CH{\cdot}CH}\\ \mathrm{NH{\cdot}CO{\cdot}C{:}N{—}CH}\end{matrix}$, is formed when β-benzoylpicolinic acid, hydrazine sulphate, and potassium hydroxide are boiled together in aqueous solution; it crystallises in white scales melting and decomposing at 236°; the *hydrochloride* forms yellow needles melting at 210—211°.

When boiled with ethyl iodide and alcoholic potash, the base yields *3-phenyl-2-ethylquinolineazone*, $\mathrm{C_{15}H_{13}ON_3}$, which crystallises in needles melting at 164°; the corresponding *methyl* derivative forms needles melting at 173—175°.

Ethyl β-benzoylpicolinate, $\mathrm{C_5NH_4Bz{\cdot}CO_2Et}$, prepared by heating an alcoholic solution of the acid in presence of sulphuric acid, crystallises in needles melting at 108—109°; the *methyl* ester forms crystals melting at 91°.

On reduction of an ammoniacal solution of β-benzoylpicolinic acid with zinc dust, *β-benzhydrylpicolinolactone*,  $\begin{matrix}\mathrm{CHPh{\cdot}C{:}CH{\cdot}CH}\\ \mathrm{O{-}CO{-}C{=}N{-}CH}\end{matrix}$, is formed; it crystallises in needles melting at 122°.

K. J. P. O.

Decomposition of Diazonium Salts by Alcohol. By ARTHUR HANTZSCH and E. JOCHEM (*Ber.*, 1901, **34**, 3337—3343. Compare Spear, Abstr., 1900, i, 703; Cameron, Abstr., 1898, i, 364).—A method is described for diazotising in acetic acid solution and separating the diazo-chloride or sulphate by precipitation with ether, which gives a theoretical yield of a much purer product than that obtained by Griess' (Abstr., 1884, 1013) or Hirsch's (Abstr., 1891, 437) method.

By methyl alcohol, benzenediazonium chloride is converted completely into anisole, no benzene being produced; the actual yield of purified anisole was 71 per cent. of the theoretical quantity. Ethyl alcohol gave a 62 per cent. yield of phenetole and a small amount of benzene. The sulphate gave, with methyl alcohol, a 69 per cent. yield of anisole, and no benzene could be isolated; with ethyl alcohol, a 58 per cent. yield of phenetole was obtained with a small amount of benzene.

p-Bromobenzenediazonium chloride gave, with methyl alcohol, an oil consisting chiefly of *p*-bromoanisole together with a smaller amount of bromobenzene, but with ethyl alcohol the product consisted entirely of bromobenzene.

p-Chlorobenzenediazonium chloride gave, with methyl alcohol, *p*-chloroanisole and a little chlorobenzene; ethyl alcohol gave an 87 per cent. yield of chlorobenzene and no chlorophenetole.

Tribromobenzenediazonium sulphate gave, with ethyl alcohol, only tribromobenzene. T. M. L.

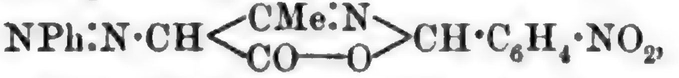
Benzeneazo-β-naphthylauramine. By RICHARD MÖHLAU and KARL P. GRAELERT (*Ber.*, 1901, **34**, 3384—3386. Compare Abstr., 1901, i, 432).—When benzeneazo-β-naphthyl-leucauramine is heated with 7 parts of alcohol as previously described, it is converted into benzeneazonaphthylauramine, but the latter undergoes further decomposition and cannot be isolated from the solution in a state of purity. This decomposition is to a large extent avoided by taking only 1·5 parts of alcohol. The *auramine*, $NPh:N\cdot C_{10}H_6\cdot N:C(C_6H_4\cdot NMe_2)_2$, is then obtained in scarlet, rhombic crystals, which exhibit a bluish surface lustre and melt at 179—180°. When heated with dilute sulphuric acid, it is quantitatively converted into benzeneazo-β-naphthylamine and tetramethyldiaminobenzophenone. A. H.

Two New Chloroanthranilic Acids. By PAUL COHN (*Chem. Centr.*, 1901, ii, 925; from *Mitt. Technol. Gewerb.-Mus. Wien*, **11**, 178—182).—The following dyes have been prepared by the action of aromatic phenols and amines on the diazo-compounds of 4- and 6-chloroanthranilic (chloro-2-aminobenzoic) acids (Abstr., 1901, i, 637). The potassium salts of the dyes have the same colour as the solutions of the sodium salts and are easily soluble in water, except in the cases mentioned. The colours of the various dyes, when dissolved in concentrated hydrochloric or sulphuric acid or in sodium hydroxide solution, are described.

The *azo-dye* prepared from 4-chloroanthranilic acid and resorcinol is a pale red powder, melts at 108°, and is easily soluble in ether. The corresponding *dye* prepared from 6-chloroanthranilic acid is a blackish-red powder, melts at 114°, and is soluble in ether. The *dye* prepared from 4-chloroanthranilic acid and salicylic acid is an orange-red powder, melts at 132°, and is very readily soluble in ether, giving a yellow solution; the *potassium* salt is scarlet. The *dye* obtained from 6-chloroanthranilic acid and salicylic acid forms brownish-yellow scales, melts at 126°, and is easily soluble in alcohol or ether; the *potassium* salt is reddish-brown and soluble in water. The *dye* prepared from 4-chloroanthranilic acid and β-naphthol is a brick-red powder, melts at 94°, and is soluble in alcohol or ether; the *potassium* salt is greenish-red with a bronze-like lustre and forms a violet solution in water. The corresponding *dye* obtained from 6-chloroanthranilic acid and β-naphthol is a lilac-red powder, melts at 89—90°, and is soluble in alcohol or ether; the *potassium* salt is violet-red and dissolves readily in water, forming a bluish-red solution. The *dye* from 4-chloroanthranilic acid and rosolic acid is a cherry-red powder, melts and decomposes at 130°, and forms a bluish-red solution in water, orange-yellow in alcohol; the *potassium* salt is slightly soluble in water. The corresponding *dye* obtained from the 6-acid is a brownish-red powder, melts and decomposes at 126°, forms a red solution in water, and is readily soluble in alcohol, giving an orange-red solution; the *potassium* salt is orange-red. The *dye* prepared from 4-chloroanthranilic acid and gallic acid is a yellowish-red powder, soluble in water or alcohol. The corresponding *dye* obtained from 6-chloroanthranilic acid is a cherry-red powder and dissolves in water, forming a cherry-red, and in alcohol, forming a pale red, solution, but is insoluble in ether.

4-Chlorosalicylic acid, prepared by boiling the diazo-compound of 4-chloroanthranilic acid, crystallises in white needles and melts at 206—207° (compare Varnholt, *J. pr. Chem.*, 1887, [ii], **36**, 27). 6-*Chlorosalicylic acid*, $OH\cdot C_6H_3Cl\cdot CO_2H$, obtained together with *m*-chlorophenol from the diazo-compound of 6-chloroanthranilic acid, crystallises in white needles, becomes red on exposure to the air, melts at 166°, is readily soluble in water and most organic solvents, is not volatile in steam, and gives a violet coloration with ferric chloride. The *ammonium* salt crystallises in brownish-yellow needles, the *potassium* salt in orange-yellow plates, and the *barium* salt in pale yellow crystals. All the preceding salts are easily soluble in water. The *silver* salt forms greyish-brown crystals and is slightly soluble in water. E. W. W.

Fatty Aromatic Aminoazo-compounds. By B. Prager (*Ber.*, 1901, **34**, 3600—3606).—Ethyl β-aminocrotonate reacts with diazobenzene chloride in acid solution to form *ethyl benzeneazoaminocrotonate*, $NHPh\cdot N{:}C(CO_2Et)\cdot CMe{:}NH$ or $NPh{:}N\cdot CH(CO_2Et)\cdot CMe{:}NH$, which crystallises in rhomb-shaped, yellow tablets melting at 102—103°. When the base is boiled with water or preserved in acid solution, ammonia is eliminated and ethyl benzeneazoacetoacetate formed. *p*-Nitrobenzaldehyde converts it into a *compound*, $C_{17}H_{14}O_4N_4$, which melts at 176—177°, probably has the constitution



$$NPh{:}N\cdot CH\genfrac{<}{>}{0pt}{}{CMe{:}N}{CO—O}CH\cdot C_6H_4\cdot NO_2,$$

and is decomposed by acids with formation of *p*-nitrobenzaldehyde and ethyl benzeneazoacetoacetate. Ethyl β-methylaminocrotonate also reacts with diazobenzene and yields *ethyl benzeneazomethylaminocrotonate*, $C_{13}H_{17}O_2N_3$, which forms large, orange-coloured crystals melting at 113—114.° This substance reacts with *p*-nitrobenzaldehyde in a different manner from the foregoing compound and yields a *substance* of the formula $C_{20}H_{22}O_5N_4$, which melts, when quickly heated, at 123—125°, and on boiling with dilute acids loses methylamine, but does not yield nitrobenzaldehyde or ethyl benzeneazoacetoacetate. Ethyl diethylaminocrotonate reacts with diazobenzene chloride, yielding a *compound*, $C_{22}H_{20}ON_5$, which is more stable than the foregoing aminoazo-compounds and forms yellow, rhomb-shaped plates, melting at 135—136°; the *hydrochloride* melts at 176—177°. This substance is accompanied by ethyl benzeneazoacetoacetate, and is probably formed from 2 mols. of diazobenzene and 1 mol. of ethyl diethylaminocrotonate. The fact that ethyl diethylaminocrotonate does not yield an aminoazo-compound with diazobenzene, whilst that obtained from ethyl methylaminocrotonate reacts with *p*-nitrobenzaldehyde in a different manner from ethyl benzeneazoaminocrotonate, indicates that the last compound has the imino- and not the true amino-formula. A. H.

[Nitrated Albumins.] By Oscar Loew (*Ber.*, 1901, **34**, 3560).—In reply to Cohnheim (*Chemie der Eiweisskörper*), it is urged that the nitrated albumins are simple derivatives of the albumins and have not undergone any complex decomposition. T. M. L.

Coagulable Components of White of Egg. By Leo Langstein (*Beitr. Chem. Physiol. Path.*, 1901, 1, 83—104).—The globulin obtained by half saturating white of egg with ammonium sulphate is probably a mixture, since it is only partially dissolved by dilute hydrochloric acid, and the soluble portion contains rather less carbon and sulphur than the original globulin. Attempts to separate globulin into components by fractional saturation with ammonium sulphate failed, however, but by treating white of egg with an equal volume of a cold saturated solution of potassium acetate, euglobulin is salted out (compare Fuld and Spiro, Abstr., 1901, ii, 67). This substance contains less carbon and nitrogen than the globulin prepared by means of ammonium sulphate, gives all the reactions of albumin, and shows Molisch's reaction especially well. By the action of dilute hydrochloric acid, it yields about 11 per cent. of glucosamine. Although the quantity of euglobulin obtained is only about two-thirds of that of the globulin prepared by ammonium sulphate, ammonium sulphate does not precipitate an albumin or pseudoglobulin (Fuld and Spiro, *loc. cit.*) from the filtrate. Egg globulin cannot be classed with the mucins (compare Eichholz, Abstr., 1898, i, 541).

Crystalline egg-albumin is to be regarded as a homogeneous compound, since it is precipitated by ammonium sulphate only between very narrow limits of concentration (62—68 per cent. saturation) and its composition is not affected by repeated recrystallisation. The non-crystalline albumin which is precipitated by heating the mother liquor contains rather less carbon but considerably more nitrogen and sulphur than the crystalline albumin; it corresponds with Osborne and Campbell's conalbumin (Abstr., 1899, i, 837; 1900, ii, 573), and when treated with dilute hydrochloric acid yields about 9 per cent. of glucosamine. The differences in the composition of crystalline egg-albumin quoted by various investigators may be partly, but cannot be wholly, due to admixture with varying amounts of conalbumin. E. W. W.

Crystalline Albumin from the White of Crows' Eggs.—By W. W. Worms (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 448—459).—By means of 2 per cent. ammonium sulphate solution, the author has isolated from the white of crows' eggs and crystallised an albumin which has been examined crystallographically by Larsky, who states that the crystals probably belong to the rhombic system. In 2 per cent. ammonium sulphate solution, the albumin has an $[\alpha]_D$ − 29·35°; in aqueous solution, when freed as far as possible from ammonium sulphate by dialysis, it has an acid reaction towards litmus, which it loses on heating or on precipitation by alcohol; it gives the xanthoprotein, Adamkiewicz, and Millon colour reactions, and, when its solution is warmed with potassium hydroxide and lead acetate, it yields a precipitate of lead sulphide. Its chemical composition is: C, 52·10; H, 7·13; N, 13·76; and S, 1·075 per cent. With acids, the albumin forms compounds the rotatory powers of which are higher than those of the albumin and are further increased on heating; thus, when dissolved in 0·1 per cent. hydrochloric acid, the value of $[\alpha]_D$ changes from −44·70° to −58·30° after heating; with 0·1 per cent. hydrobromic acid, the increase is from −36·30° to −53·35°, and with 0·5 per cent. phosphoric acid from −33·30° to −51·25°. The following table gives the composition of the crystalline albumins obtained by Panormoff from the whites of hens' and pigeons' eggs (Abstr., 1900, i, 126, 127, 571, 709), and of that now described by the author:

	Hen.	Pigeon.	Crow.
C	52·97	52·06	52·10
H	7·28	7·12	7·13
N	15·10	13·28	13·69
S	1·63	1·07	1·08

These numbers show the great similarity in composition between the compounds obtained from pigeons' and crows' eggs, although they are not identical, as is shown by differences in composition of the derivatives formed with hydrochloric and hydrobromic acids.

T. H. P.

Carbohydrates of Crystallised Serum-Albumin. By Leo Langstein (*Beitr. Chem. Physiol. Path.*, 1901, 1, 259—268).—There appear to be two carbohydrate components derivable from crystallised serum-albumin; one is glucosamine, the second is a substance which yields furfuraldehyde and an acid similar to saccharic or gulonic acid; its nature is, however, not definitely settled. W. D. H.

Crystalline Albumin from the Serum of Horses' Blood. By Stephan Maximowitsch (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 460—469).—The author has obtained a crystalline albumin from horses' blood by the following method. The defibrinated arterial blood was mixed with an equal volume of saturated ammonium sulphate solution to separate the paraglobulin, &c. After filtering, the clear liquid was mixed with sufficient saturated aqueous ammonium sulphate to make it just turbid, and kept, when it gradually deposited a precipitate which was partly crystalline and partly amorphous and was purified by repeated recrystallisation from ammonium sulphate solution. In 2 per cent. ammonium sulphate solution, the albumin has

$[\alpha]_D$ +47·47° at 20°, the value for an aqueous solution being 47·30°. The pure, salt-free albumin has the percentage composition: C, 53·06; H, 7·05; O, 22·31; N, 15·69; S, 1·89.

The compound formed by the albumin with hydrochloric acid, the composition of which is unchanged by heating, has, in a 0·1 per cent. hydrochloric acid solution, $[\alpha]_D$ 65·065° before heating and 72·22° after heating. Similarly, the rotation of the hydrobromic acid compound is changed from $[\alpha]_D$ 63·80° before heating to 69·13° afterwards, whilst in the case of the phosphoric acid compound the values are 62·2° and 67·87° respectively. The elementary composition of the author's albumin agrees well with the formula proposed by Kuraeff for serum-albumin, namely, $C_{225}H_{360}O_{70}N_{58}S_3$, the percentage composition of which is: C, 53·07; H, 7·07; O, 22·01; N, 15·96, and S, 1·89. Taking this formula for the albumin prepared by the author and representing the molecule by Alb, the compounds formed with mineral acids agree well in composition with the formulæ: Alb,6HCl; 2Alb,9HBr, and $Alb,4H_3PO_4$. T. H. P.

Globulin as Alkali Proteid. By L. K. Wolff and A. Smits (*Zeit. Biol.*, 1901, **41**, 437—443).—The experiments which led Starke (Abstr., 1901, i, 242) to conclude that globulins are alkali-proteids are criticised, especially those of a physico-chemical nature. W. D. H.

Tendon Mucoid. By W. D. Cutter and William J. Gies (*Amer. J. Physiol.*, 1901, **6**, 155—172).—The term mucoid is adopted instead of mucin, which is reserved for gluco-proteids elaborated by secretory cells. There is more than one gluco-proteid in tendon. Analyses of five preparations of the mixed mucoids are given, the principal point of interest in which is the relatively high percentage of sulphur (2·3). The average composition and heat of combustion of the mucoids are nearly the same as those found in the mucoids separated from bone and cartilage. W. D. H.

Green Colouring Matter from the Blood of Animals Poisoned by Phenylhydrazine By Louis Lewin (*Compt. rend.*, 1901, **133**, 599—601).—The blood of warm blooded or cold blooded animals poisoned by phenylhydrazine or its hydrochloride resembles an emulsion, and is reddish-brown by reflected light and green by transmitted light. When heated with acids, it becomes green and resembles chlorophyll. The blood contains a green, amorphous substance, *hæmoverdin*, soluble in alcohol, paraldehyde or acetone, and slightly so in ether, but insoluble in chloroform. It can be obtained, but in small quantity only, by the direct action of phenylhydrazine on defibrinated blood, and is probably a product of the alteration of hæmoglobin. It is not formed when animals are poisoned by aniline, *p*-aminophenol, diazobenzene, and hydrazine sulphate or hydrate. The spectrum of hæmoverdin shows a broad absorption band beginning at *D* and extending towards the violet, a narrow band one-third of the distance from *C* to *D*, a narrow band two-thirds of the distance from *C* to *D*, and a fourth band half-way between *D* and *E*, with considerable general absorption in the blue. C. H. B.

Suprarenin. By Otto von Fürth (*Beitr. Chem. Physiol. Path.*, 1901, 1, 243—251. Compare Abstr., 1900, ii, 242).—Some further facts are added in connection with the benzoyl and other compounds of suprarenin. It is claimed that suprarenin is identical with Takamine's adrenalin. W. D. H.

Pentahalogen Compounds of Antimony and their Double Compounds. By Arthur Rosenheim and Wilhelm Stellmann (*Ber.*, 1901, **34**, 3377—3384).—Antimony pentachloride unites with pyridine hydrochloride to form a salt which crystallises in brownish-golden, lustrous needles and is decomposed by water. The corresponding salts with the hydrochlorides of quinoline and dimethylaniline are colourless. Double salts of antimony pentabromide (which will itself be described in a further communication) have been obtained by adding pyridine hydrobromide to the product of the action of ethereal hydrogen bromide on antimonic acid. A mixture is thus obtained of a *double* salt of antimony tribromide, $2C_5NH_5,HBr,SbBr_3$, crystallising in yellow, lustrous needles, with a *double* salt of the pentabromide, $2C_5NH_5,HBr,SbBr_5$, crystallising in black plates, whilst in presence of a few drops of bromine only the black crystals are formed. The corresponding salts of quinoline and dimethylaniline form yellowish-white needles.

Antimony pentachloride forms compounds with many organic oxygen derivatives, some of which are well known (Williams, this Journ., 1876, ii, 463). With acetaldehyde, it forms the *compound*,

$$SbCl_5,CH_3{\cdot}CHO,$$

which crystallises in druses of yellowish-white needles. The *compound* with benzaldehyde also crystallises in needles, whilst that with *acetone* forms large, very hygroscopic, prisms. With ethyl benzoate it forms a *compound*, $SbCl_5,Ph{\cdot}CO_2Et$, crystallising in lustrous, rhombic tablets; the *compound* with benzoyl chloride, $2SbCl_5,3COPhCl$, crystallises in needles, the *compound* with acetamide, $2SbCl_5{\cdot}3COMe{\cdot}NH_2$, forms hygroscopic, crystalline crusts, and the *compound* with phthalic anhydride, $2SbCl_5,3C_6H_4{:}C_2O_3$, also crystallises in extremely hygroscopic crusts. Antimony pentachloride also unites with many organic acids; with oxalic acid, it forms a *compound*, $2SbCl_5,C_2H_2O_4$, which crystallises in prisms. When this substance is heated with oxalic acid, the free oxalic acid is oxidised and half of the pentachloride reduced. The product of this reaction has been described by Anschütz and Evans (*Annalen*, 1887, **239**, 293) as ditetrachlorostibonium oxalate. With nitrobenzene, the pentachloride yields yellow *needles* of the composition $2SbCl_5,3Ph{\cdot}NO_2$. The pentachloride appears to react more violently when the oxygen compound contains an ethylene linking, as is the case with cinnamaldehyde. It yields no compounds with hydrocarbons, hydrogen chloride being always evolved and a chloro-derivative and antimony trichloride formed, double salts of the latter being then produced. Thus the action of the pentachloride on benzene gives rise to the *compound* $3SbCl_3,C_6H_6$, which crystallises in prisms; an analogous compound is formed with toluene. A. H.

Organic Chemistry.

Substitution Process in the Fatty Series. By ARTHUR MICHAEL [with W. H. GRAVES and W. W. GARNER] (*Ber.*, 1901, **34**, 4028—4060).—The process of substitution in the fatty series is discussed, and recognising that the principal factors in the replacement of hydrogen by chlorine and bromine are the chemical attraction between the hydrogen atom, which is replaced, and the halogen, on the one hand, and between the halogen and carbon atoms on the other, the author considers that the presence of positive groups (methyl, &c.) renders greater the attraction between the carbon and hydrogen, whilst negative groups (carbethoxy, &c.) loosen this linking; further, positive groups attract to, and negative groups repel from, their neighbourhood negative substituents.

The bromination of hexane in sunlight leads mainly to the formation of β- and γ-bromohexanes, together with a small quantity of α-bromohexane and a dibromohexane. By conversion of the β- and γ-bromohexanes into the corresponding hexanones (Abstr., 1900, i, 321), it was shown that the quantity of the β-compound is considerably greater than that of the γ-compound.

At its boiling point, ethyl α-bromobutyrate is said to be converted into ethyl β-bromobutyrate (Erlenmeyer and Marx). It is found, however, that after many distillations of the pure α-bromo-ester, less than 1½ per cent. is converted into the β-derivative. The boiling point of pure ethyl α-bromobutyrate is 177·5° at 764·6 mm. pressure.

α-Bromo*iso*butyric acid is not transformed into the β-bromo-acid at 100°; the corresponding ester is only transformed to a very small extent after boiling for 2 hours.

α-Bromopropionic acid can be distilled under the ordinary pressure without undergoing any change; when heated for many hours at 120—130° under pressure, a small amount of β-bromopropionic acid is formed. Ethyl α-bromovalerate distils unchanged at 193—196° after having been boiled.

The chlorides of several fatty acids were chlorinated by a 10 per cent. solution of chlorine in carbon tetrachloride and the resulting products fractionated under reduced pressure. Propionyl chloride yielded mainly (at least 65 per cent.) *β-chloropropionyl chloride*,

$$CH_2Cl\cdot CH_2\cdot COCl,$$

an oil boiling at 82—82·5° (corr.) under 102 mm. pressure, together with a smaller quantity of the α-chloro compound. It is noticeable that α-chloropropionic acid yields some acrylic acid under the action of alkalis, whilst α-bromopropionic acid gives only traces.

On chlorination of butyryl chloride, β-chlorobutyryl chloride forms 60 per cent. of the product, and the α- and γ-chloro-derivatives each about 20 per cent.; at the same time, some *αγ-dichlorobutyryl chloride* $CH_2Cl\cdot CH_2\cdot CHCl\cdot COCl$, is produced as an oil boiling at 98—100° under 42 mm. pressure, and yielding a chlorobutyrolactone when converted into the corresponding acid and the latter subjected to dry distillation.

β-Chlorobutyranilide, $CHMeCl\cdot CH_2\cdot CO\cdot NHPh$, prepared from aniline and β-chlorobutyryl chloride, crystallises in thin leaflets melting at 89—90°.

*iso*Butyryl chloride yields 60—70 per cent. of the α-chloro- and 30—40 per cent. of the β-chloro-derivative. *α-Chloro*iso*butyranilide*, $CClMe_2\cdot CO\cdot NHPh$, crystallises in thin leaflets melting at 69—70°, and *β-chloro*iso*butyranilide* in leaflets melting at 104—105°.

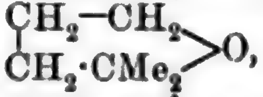
From *iso*valeryl chloride, β-chloro*iso*valeryl chloride is obtained as the chief product, whilst both the α- and γ-chloro-derivatives are formed in smaller quantity.

Bromine and *iso*butyryl chloride give mainly the α-bromo-, together with a little of the β-bromo-derivative. When bromine and *iso*butyryl chloride in mol. proportion were exposed to sunlight, bright red crystals separated of a *substance* which melted at 40—42°, did not contain chlorine, and in the air readily decomposed, giving bromine and hydrogen bromide. On being dried in a desiccator over phosphoric oxide, it became white.

Two pieces of apparatus are described in the paper, which are especially adapted to the fractionation of the substances dealt with.

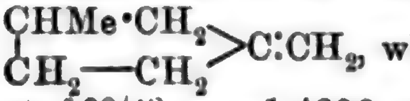
K. J. P. O.

Isomerisation of Dimethyl*cyclo*propylcarbinol. By NICOLAI D. ZELINSKY (*Ber.*, 1901, **34**, 3887—3889).

—On heating *cyclo*propyldimethylcarbinol (Abstr., 1901, i, 660) with crystallised (hydrated) oxalic acid, a *substance*, $C_6H_{12}O$, was obtained as an oil with a pleasant odour, which readily distilled with steam, boiled at 92—93° under 746 mm. pressure, and had a sp. gr. 0·835 at 21°/4° and $[n]_D$ 1·4063 at 21°. The same substance was formed when anhydrous oxalic acid was used. It proves to be a hexylene oxide,  $\left.\begin{array}{l}CH_2-CH_2\\ CH_2\cdot CMe_2\end{array}\right>O$, and is probably formed by addition of the elements of water and a consequent opening of the methylene ring, followed by elimination of water with the production of the oxide.

K. J. P. O.

Syntheses of Cyclic Tertiary Alcohols by means of Organomagnesium Compounds. By NICOLAI D. ZELINSKY [and J. GUTT] (*Ber.*, 1901, **34**, 3950—3952).

—The following compounds have been obtained by Grignard's methods (Abstr., 1900, i, 382). 1 : 3-*Dimethyl*cyclo*pentanol*-3 (from 1-methyl*cyclo*pentanone-3) boils at 88·5—89° under a pressure of 94 mm., or at 143—145° under atmospheric pressure, not, however, without some decomposition; it has a sp. gr. 0·8935 at 19°/4°, n_D 1·4434 at 19°, and α 1·49° when $l = 0{\cdot}25$ dcm. When treated with oxalic acid, it yields the unsaturated *hydrocarbon*,  $\left.\begin{array}{l}CHMe\cdot CH_2\\ CH_2-CH_2\end{array}\right>C{:}CH_2$, which boils at 93·5° (corr.), has a sp. gr. 0·7734 at 19°/4°, n_D 1·4296 at 19°, $[\alpha]_D$ 57·67°, and when oxidised with potassium permanganate yields 1-methyl*cyclo*pentanone-3. 1-*Methyl*-3-*ethyl*cyclo*pentanol*-3, boils at 71° under a pressure of 21 mm., and has a sp. gr. 0·8974 at 19°/4°.

R. H. P.

Partially Acetylated Polyhydroxylic Compounds. Knoll & Co. (D.R.-P. 122145).—When completely acetylated hydroxylic compounds are heated with the unaltered substance, a reaction occurs between the two, resulting in the formation of a partially acetylated derivative. When triacetin and glycerol in equal proportion by weight are heated for several hours at 200°, the chief product of reaction is monoacetin. Monoacetylresorcinol results from resorcinol (2 parts) and diacetylresorcinol (3 parts) when the mixture is heated at 170°. The monoacetyl derivative of pyrogallol is produced under similar conditions from a mixture of pyrogallol and its triacetyl compound. Anthrapurpurin and its triacetyl compound yield the corresponding diacetyl derivative. G. T. M.

Dihydroxy*iso*propyl*hypo*phosphorous Acid. By Ch. Marie (*Compt. rend.*, 1901, **133**, 818—820. Compare Abstr., 1901, i, 635).—*Dihydroxyisopropylhypophosphorous acid*, $PO_2H_3,(C_3H_6O)_2$, melts at 185—186° and loses acetone when heated at 150°, or when boiled with strong acids or alkalis. Mercuric chloride does not oxidise the acid in the cold, but when boiled converts it into an acid, PO_2H_3,C_3H_6O; lead oxide similarly gives the lead salt of the last-mentioned acid.

The salts of dihydroxy*iso*propylhypophosphorous acid are all soluble in water, and are easily prepared from the acid and the oxide or carbonate of the metal. The *sodium* salt, $(C_3H_6O)_2,PO_2H_2Na,3H_2O$, forms colourless, efflorescent crystals soluble in alcohol; the *lead* salt crystallises with $2H_2O$; the *silver* salt forms anhydrous, delicate needles, sensitive to light; the *lanthanum* and *cerium* salts are anhydrous and much less soluble in hot than in cold water. The *methyl* and *ethyl* esters are prepared from the silver salt and alkyl iodide and form colourless crystals which melt respectively at 92° and 95°. A *diacetyl* derivative, $(C_3H_6O)_2,PO_2HAc_2$, melting at 171° is obtained when the acid is treated with acetic anhydride. The *dibenzoyl* derivative, $(C_3H_6O)_2,PO_2HBz_2$, was prepared by dissolving the acid in excess of pyridine and slowly adding an ethereal solution of benzoyl chloride; it melts at 195—196° and is a monobasic acid. The *silver* salt, $(C_3H_6O)_2,PO_2AgBz_2$, is an insoluble, crystalline powder. The *methyl* and *ethyl* esters were obtained from the silver salt as amorphous masses.

The formula $PO(CMe_2\cdot OH)_2\cdot OH$ is suggested for the acid (compare Ville, Abstr., 1889, i, 1134). K. J. P. O.

Reactions of Trichloroacetic Acid. By Arthur Clermont (*Compt. rend.*, 1901, **133**, 737—738).—When mol. proportions of trichloroacetic acid, alcohol, and sulphuric acid are mixed, heat is developed and the liquid becomes opalescent. On adding water, ethyl trichloroacetate separates as an oil. Addition of its own volume of ammonia to the oil rapidly converts it into *trichloroacetamide*, which sublimes in plates resembling naphthalene, melts at 135°, and boils at 240°.

The ready formation of the ester is suggested, as a means of recognising trichloroacetic acid in the presence of other chloro-acids.

K. J. P. O.

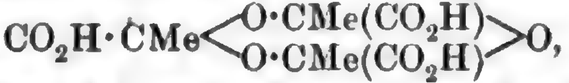
Montan Wax. By Edgar von Boyen (*Zeit. angew. Chem.*, 1901, **14**, 1110—1111).—Montan wax is a hard, crystalline wax melting at about 70° and is obtained when bitumen from brown coal is subjected to steam distillation. It appears to be a mixture of montanic acid, $C_{29}H_{58}O_2$ (compare Hell, *Zeit. angew. Chem.*, 1900, **13**, 556), and an alcohol. The alcohol is easily soluble in light petroleum, melts at 60°, and is readily attacked by sulphuric or nitric acid. The original bitumen is probably an ester of the alcohol and acid and is hydrolysed during distillation with steam.

Potassium and *sodium montanates* are readily soluble in hot water, but yield gelatinous precipitates on the addition of much water.

The *magnesium* salt crystallises from alcohol in needles

J. J. S.

Transformation of Salts of Pyruvic Acid. By A. W. K. de Jong (*Rec. Trav. Chim.*, 1901, [ii], **20**, 365—387. Compare Wolff, Abstr., 1899, i, 483).—Careful analyses of barium parapyruvate (W) (Wolff's salt) agree best with the formula $(C_6H_6O_6Ba,4H_2O)_n$; the salt is decomposed by boiling water to form the soluble *barium metapyruvate*, which, with phenylhydrazine hydrochloride, gives nearly the theoretical quantity of the phenylhydrazone of pyruvic acid. As barium parapyruvate loses exactly $3\frac{1}{3}H_2O$ when exposed over sulphuric acid, it is probable that the salt has the molecular composition $(C_6H_6O_6Ba)_3,12H_2O$, and is derived from the product



$$\mathrm{CO_2H\cdot CMe}<\begin{matrix}\mathrm{O\cdot CMe(CO_2H)}\\ \mathrm{O\cdot CMe(CO_2H)}\end{matrix}>\mathrm{O},$$

of the polymerisation of 3 mols. of pyruvic acid. The metapyruvates are possibly derived from the simpler form, $\mathrm{CO_2H\cdot CMe}<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}>\mathrm{CMe\cdot CO_2H}$.

The barium parapyruvate, obtained by the action of dilute aqueous potassium cyanide or potassium hydroxide on barium pyruvate according to Wolff's method, is always slightly impure, containing barium carbonate and another barium salt; it does not completely dissolve on boiling with water, although the purer barium parapyruvate, obtained by transforming barium pyruvate by means of a very small quantity of barium hydroxide, readily does so. Finck's so-called basic barium salt, $(C_9H_9O_9)_2Ba_3,Ba(OH)_2$, is merely a mixture of the impure parapyruvate with barium carbonate and hydroxide.

A large part of the paper deals with the method of purifying barium parapyruvate and the quantitative estimation of pyruvic acid in the form of its phenylhydrazone. W. A. D.

Intramolecular Migration of Acyl Groups. By Wilhelm Wislicenus and Heinrich Körber (*Ber.*, 1901, **34**, 3768. Compare Abstr., 1901, i, 187).—The conversion of ethyl *O*-acetylacetoacetate into ethyl diacetoacetate at high temperatures is best carried out at 240°, but even then the yield is only 1 per cent. of the theoretical. At 260°, the yield is doubled, but a considerable amount of acetylacetone is produced. The two compounds are identified by means of their copper derivatives.

G. T. M.

Action of certain Acid Chlorides on Methyl and Ethyl Sodioacetoacetate. By A. Bongert (*Compt. rend.*, 1901, **133**, 820—821. Compare Abstr., 1901, i, 311).—*Ethyl propionylacetoacetate* (*C*-ester), $CMeO\cdot CH(CEtO)\cdot CO_2Et$, formed together with the *O*-ester by the action of propionyl chloride on ethyl sodioacetoacetate, is a colourless oil boiling at 112—113° under 20 mm. pressure, having a sp. gr. 1·091 at 0°/4°, and giving a red coloration with ferric chloride; the *copper* salt crystallises in blue needles melting at 78°. The O-*ester* is separated from the *C* ester by means of a saturated solution of sodium carbonate, and is a colourless oil boiling at 121° under 23 mm. pressure and having a sp. gr. 1·061 at 0°/4°; it gives no coloration with ferric chloride. The *C*-ester represents 59 per cent. of the mixed esters.

Ethyl C-*butyrylacetoacetate*, $CMeO\cdot CH(CPr^{\alpha}O)\cdot CO_2Et$, is a colourless liquid which boils at 112° under 16 mm. pressure, has a sp. gr. 1·062 at 0°/4°, and represents 56 per cent. of the mixed esters; its *copper* salt forms blue needles melting at 89°. The O-*ester* boils at 112—113° under 10 mm. pressure and has a sp. gr. 1·033 at 0°/4°. With dry ammonia, the *C*-ester yields acetamide and ethyl butyrylacetate (compare Blaise, Abstr., 1901, i, 363), which boils at 101° under 20 mm. pressure and has a sp. gr. 1·007 at 0°.

Methyl C-iso*valerylacetoacetate*, $CMeO\cdot CH(CH_2Pr^{\beta}\cdot CO)\cdot CO_2Me$, is a colourless oil boiling at 107—108° under 11 mm. pressure and has a sp. gr. 1·069 at 0°/4°; its *copper* salt crystallises in opalescent, blue needles melting at 137°. When heated with water at 140—150° under pressure, the ester decomposes into carbon dioxide, methyl alcohol, and iso*valerylacetone*, $CMeO\cdot CH_2\cdot CO\cdot CH_2Pr^{\beta}$, which is a colourless liquid with a fruity odour boiling at 76° under 19 mm. pressure and having a sp. gr. 0·936 at 0°/4°; the *copper* salt forms small, blue crystals melting at 142°. With dry ammonia, the ester yields acetamide and *methyl* iso*valerylacetate*; the latter boils at 95° under 19 mm. pressure and has a sp. gr. 1·006 at 0°/4°; the *copper* salt forms small, green crystals melting at 136°. The last-mentioned methyl ester gives, with hydrazine, 3-iso*butylpyrazolone*, which crystallises in white spangles melting at 229°. *Methyl* O-iso*valerylacetoacetate* is a colourless oil of disagreeable odour boiling at 113—114° under 11 mm. pressure, and having a sp. gr. 1·039 at 0°/4°.

Methyl C-*hexoylacetoacetate*, $CMeO\cdot CH(CO\cdot[CH_2]_3\cdot CH_2Me)\cdot CO_2Me$, is a colourless liquid boiling at 144° under 21 mm. pressure and having a sp. gr. 1·056 at 0°/4°; its *copper* salt crystallises in opalescent blue needles melting at 92°; the corresponding O-*ester* boils at 142° under 16 mm. pressure and has a sp. gr. 1·026 at 0°/4°. When heated with water at 140—150° under pressure, the *C*-ester yields carbon dioxide, methyl alcohol, and hexoylacetone, which is a colourless oil with a fruity odour, melting at –18°, boiling at 98—100° under 20 mm. pressure, and having a sp. gr. 0·936 at 0°/4°; it is identical with the diketone obtained by Moureu and Delange (Abstr., 1901, i, 14); the *copper* salt forms small, blue, opalescent crystals melting at 134°.

With ammonia, methyl *C*-valerylacetoacetate gives acetamide and *methyl hexoylacetate*, $CH_2Me\cdot[CH_2]_3\cdot CO\cdot CH_2\cdot CO_2Me$; the latter is an oil boiling at 118° under 19 mm. pressure and having a sp. gr. 0·991 at 0°/4°; with hydrazine, 3-*amylpyrazolone* is formed as white plates melting at 195°. K. J. P. O.

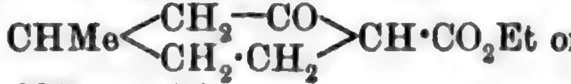
The Red Alkali Chromo-oxalates. By ARTHUR ROSENHEIM and ROBERT COHN (*Zeit. anorg. Chem.*, 1901, **28**, 337—341. Compare Abstr., 1896, i, 278).—Crystals of the red chromo-oxalates, obtained by treating a saturated solution of chromium hydroxide with 3 mols. of oxalic acid and 1 mol. of normal alkali oxalate, lose water at 110° and change their habit. Further heating at 140° expels no more water, but above this temperature more water is lost. The compounds contain 2 mols. of water of constitution and are dioxalatodiaquochromates, $[Cr(C_2O_4)_2(H_2O)_2]K,3H_2O$, $[Cr(C_2O_4)_2(H_2O)_2]NH_4,3H_2O$; $[Cr(C_2O_4)_2(H_2O)_2]Na,5H_2O$. Treated with 20 per cent. ammonia (2 mols. NH_3 : 1 mol. red salt), the crystals liquefy, and if the liquid be warmed until the smell of ammonia disappears, light green crystals of chromamminoxalates separate on cooling.

The silver-grey salt prepared by Wyrouboff (Abstr., 1901, i, 579) contains 16 mols. of water (not 13), $Cr_2(C_2O_4)_3,16H_2O$, of which 6 mols. are water of constitution. This may be a hydrate of trioxalatohexaquodichromium, $[Cr_2(C_2O_4)_3(H_2O)_6],10H_2O$, which would be a non-ionising compound, but since a change in properties takes place on heating, it is possible that the non-ionising compound is the known non-crystallising violet chromic oxalate. J. McC.

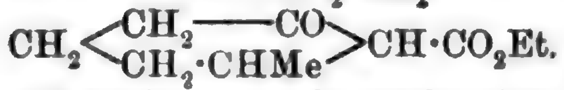
1-Methyl*cyclo*hexane-3-malonic Acid and 1-Methyl*cyclo*hexane-3-acetic Acid. By NICOLAI D. ZELINSKY and D. ALEXANDROFF (*Ber.*, 1901, **34**, 3885—3889).—*Ethyl* 1-*methyl*cyclo*hexane-3-malonate*, $C_6H_{10}Me\cdot CH(CO_2Et)_2$, is formed when a mixture of ethyl malonate and 3-bromo-1-methyl*cyclo*hexane is treated with sodium; it is a colourless oil boiling at 150—154° under 10—12 mm. pressure, and has $[\alpha]_D - 3·94°$. The corresponding *acid*, $C_{10}H_{16}O_4$, obtained by boiling the ester with alcoholic potassium hydroxide, forms crystals melting at 143—144°; at the same time, a second isomeric *acid*, $C_{10}H_{16}O_4$, is formed, which crystallises in small stars melting and decomposing at 121—122°. From these facts, two stereoisomeric 1-methyl*cyclo*hexane-3-malonic acids appear to exist. On heating the acid with the melting point 143—144° at 160°, 1-*methyl*cyclo*hexane-3-acetic acid*, $C_6H_{10}Me\cdot CH_2\cdot CO_2H$, is formed as a liquid with the characteristic odour of a fatty acid, boiling at 144° under 19—20 mm. pressure and having a sp. gr. 0·9827 at 21°/4° and $[n]_D$ 1·4582 at 21°.

Ethyl 1 : 1′-*di-methyl*cyclo*hexanemalonate*, $(C_6H_{10}Me_2)_2C(CO_2Et)_2$, is formed together with the ester just described, and is a liquid boiling at 200—205° under 8—10 mm. pressure. K. J. P. O.

Derivatives of β-Methylpimelic Acid. By ALFRED EINHORN and LUDWIG KLAGES (*Ber.*, 1901, **34**, 3793—3798. Compare Abstr., 1897, i, 344).—Ethyl β-methylpimelate, when heated with sodium, somewhat above 100°, yields the sodium salt of *ethyl methyl-2-ketohexamethylenecarboxylate.* The *ester*, obtained from the sodium salt, is a colourless oil, with an odour resembling that of ethyl acetoacetate, and boils at 145—150° under a pressure of 29 mm.; in alcoholic solution it gives a blue coloration with dry, a deep violet with moist, ethereal ferric chloride, and a red with aqueous ferric chloride. The ester has either the constitution



$CHMe<\begin{smallmatrix}CH_2-CO\\CH_2\cdot CH_2\end{smallmatrix}>CH\cdot CO_2Et$ or



$CH_2<\begin{smallmatrix}CH_2-\!\!-\!\!-CO\\CH_2\cdot CHMe\end{smallmatrix}>CH\cdot CO_2Et$.

Ethyl methylisopropyl-2-ketohexamethylenecarboxylate, $C_{13}H_{22}O_3$, prepared by the action of sodium on a mixture of *iso*propyl iodide and the ester just mentioned, is a colourless oil boiling at 165—168° under 20 mm. pressure. When this ester is boiled with excess of concentrated alcoholic potash, a methyl*iso*propylketohexamethylene (b. p. 204—206°) is formed, which is probably identical with inactive menthone (Urban and Kremers, Abstr., 1894, i, 468), as it has the same boiling point and yields an oxime with the same melting point (78—80°).

K. J. P. O.

Optical Rotations of Certain Tartrates in Glycerol. By John H. Long (*J. Amer. Chem. Soc.*, 1901, **23**, 813—817).—The rotatory power of a number of tartrates in water and in glycerol at 20° has been determined with the following results:

Salt.	$[\alpha]_D$ for water.	$[\alpha]_D$ for glycerol.
$KNaC_4H_4O_6,4H_2O$	22·1° $c=5$ to 30	28·85° $c=5$
		28·35 $c=10$
		27·87 $c=15$
		27·40 $c=20$
		26·96 $c=25$
$KSbOC_4H_4O_6,\frac{1}{2}H_2O$	140·69 $c=2$	139·25 $c=2$
	141·27 $c=5$	141·17 $c=3$
	141·40 $c=6$	143·75 $c=4$
$K(BO)C_4H_4O_6$	58·10 $c=5$	30·9 $c=5$
$(NH_4)_2C_4H_4O_6$	34·50 $c=5$	43·50 $c=4$
$NH_4HC_4H_4O_6$	26·0 $c=1·5$	27·7 $c=0·75$
$NH_4(SbO)C_4H_4O_6,\frac{1}{2}H_2O$ ...	150·0 $c=5$	146·10 $c=3$
		146·25 $c=4$
$NH_4(SbO)C_4H_4O_6,2\frac{1}{2}H_2O$ ...	115·7 $c=5$	109·37 $c=4$

These determinations show that the simple metallic tartrates examined have a higher specific rotatory power in glycerol than in water. The antimonyl tartrates have nearly the same rotation in water and glycerol, and their behaviour in general suggests a constitution different to that usually assigned to these salts. Potassium borotartrate has a lower rotatory power in glycerol than in water, probably due to the withdrawal of part or the whole of the boric radicle to form a glycerol compound.

E. G.

Action of Ammonium Paramolybdate on the Specific Rotation of Sodium Hydrogen Tartrate. By Peter Klason and John Köhler (*Ber.*, 1901, **34**, 3946—3949).—The results of Itzig (Abstr., 1901, i, 448) require correction in accordance with the researches of Klason on molybdates (Abstr., 1901, i, 162). The rule formulated by Rosenheim and Itzig (Abstr., 1900, i, 272) is wrong, as the maximum rotation given by sodium hydrogen tartrate depends, not only on the proportion of alkali ions to tartrate ions, but also on the molybdic acid, the concentration, and the temperature. R. H. P.

Complex Derivatives of Uranic Acid. By HERRMANN ITZIG (*Ber.*, 1901, **34**, 3822—3827).—The great increase in the optical rotation of malic and tartaric acids in the presence of uranyl salts is to be attributed to the formation of complex urani-organic compounds (Walden, Abstr., 1898, ii, 149). Peligot's uranyl tartrate (*Annalen*, 1845, **56**, 231, and Dittrich, Abstr., 1899, ii, 629) is not a salt, its molecular weight is normal, its dissociation factor is 0·03 per cent., and its molecular rotation lies between +404° and 410°. The constitution suggested is $CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot O\cdot UrO_2\cdot OH$, *uranotartaric acid*. It forms a *potassium* salt which has only been obtained in solution and has a molecular rotation 500° to 511°; on exposure to light, the solution rapidly turns brown. Potassium, barium, and calcium chlorides do not yield precipitates with these complex tartrates. *Uranomalic acid*, $CO_2H\cdot CH_2\cdot CH(OH)\cdot CO\cdot O\cdot UrO_2\cdot OH$, has a molecular rotation −460° to −467°, and yields a *sodium* salt, $C_4H_5O_8UrNa,2H_2O$, with a molecular rotation −682° to −686°.

J. J. S.

Methylene Compounds of Hydroxy-acids. By CORNELIS A. LOBRY DE BRUYN and WILLIAM ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1901, **20**, 331—343).—Most of the facts of this paper have previously been dealt with (Abstr., 1901, i, 120).

The compounds previously described are better obtained by heating the hydroxy-acids with dry, powdered trioxymethylene in chloroform solution for several hours at 150°; in some cases, the addition of anhydrous sodium sulphate is advantageous.

The *derivative* of *l*-tartaric acid melts at the same temperature (116—117°) as that of the *d*-acid; the racemic acid *derivative*, which could not be obtained formerly, crystallises well and melts at 103°. Lactic, glycollic and glyceric acids yield *oily* derivatives, and saccharic acid an oil containing three formal groups and having $[\alpha]_D$ +62° in a 4 per cent. methyl alcoholic solution; the triformal derivative of *l*-gulonic acid is an oil with $[\alpha]_D$ −48°.

d-Tartaric acid, when heated for 2 hours at 150° with paraldehyde and sodium sulphate in chloroform, yields a small quantity (3 per cent.) of a *diacetal* derivative, which forms needles, melts at 121°, and has $[\alpha]_D$ about +82 in a 1 per cent. methyl alcoholic solution. Citric acid yields similarly, at 120°, an acetal derivative melting at 180°.

W. A. D.

Bismuth Compounds derived from Organic Acids and employed in Pharmacy. By LÉON PRUNIER (*J. Pharm. Chim.*, 1901, [iv], **14**, 493—499. Compare Abstr., 1901, i, 593; ii, 106).—The crystalline compounds of bismuth with organic acids may be divided into two groups. The compounds belonging to the first group are true bismuth salts such as bismuth salicylate, lactate, and malate and normal bismuth citrate. The second group includes those compounds which possess acid properties and form salts with potassium, sodium, and ammonium. In the latter compounds, the bismuth does not play the part of a base but rather that of an acid, so that they must be regarded as bismuthic organic acids. To this class belong bismuthiditartaric acid and the so-called basic bismuth gallate, which is really bismuthigallic acid. H. R. Le S.

Reduction-potential of Aldehydes. By E. Baur (*Ber.*, 1901, **34**, 3732—3735).—The maximum value of the reduction-potential of formaldehyde (2 c.c. of 40 per cent. formalin with 50 c.c. of *N* sodium hydroxide) was found to be -0.343 volt, that of acetaldehyde (2 c.c. with 50 c.c. of *N* sodium hydroxide) -0.238 volt; that of benzaldehyde could not be satisfactorily measured owing to the slight solubility of the substance. The aldehydes thus act as powerful depolarisers at the anode, where they are oxidised to acids; when sodium hydroxide was electrolysed between platinum plates the current was increased more than 100-fold by adding formaldehyde in the anode compartment. The aldehydes are also capable of acting as depolarisers at the cathode by becoming reduced to alcohols, but this change proceeds only slowly and does not prevent the liberation of hydrogen. T. M. L.

Action of Hydrogen Chloride on Aqueous Formaldehyde. By G. H. Coops (*Rec. Trav. Chim.*, 1901, **20**, 267—289).—Contrary to Lösekann's statement (*Chem. Zeit.*, 1890, **14**, 1408), the product of this action is not chloromethyl alcohol but a mixture of this with the two substituted *ethers*, $OH\cdot CH_2\cdot O\cdot CH_2Cl$ and $OH\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot CH_2Cl$; it is not possible, as formerly stated, to separate the chloromethyl ether by simply distilling off the portion boiling below 85° and then washing the residue with water, and the part boiling between 45—85° is not the ether $CH_2Cl\cdot O\cdot CH_2\cdot OH$.

The unpurified oily product of the action of hydrogen chloride on formaldehyde is decomposed by an excess of water giving trioxymethylene, formed by elimination of 1 HCl from $OH\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot CH_2Cl$; cold aqueous potassium hydroxide yields only formaldehyde but on warming methyl alcohol and formic acid are produced from the latter.

The action of alcohol on the original product develops considerable heat and gives a mixture of diethoxymethane boiling at 86—90°, and having a sp. gr. 0·840, *diethoxydimethyl ether*, $(OEt\cdot CH_2)_2O$, which boils at 102—106° and has a sp. gr. 0·864, and the *substance*, $OEt\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot CH_2Cl$ which has a sp. gr. 1·02 and distils at 47° under 30 mm. pressure, producing considerable quantities of formaldehyde. The first two substances cannot be isolated by direct fractionation of the product of the action of alcohol, but are easily separated by treating this with potassium hydroxide or carbonate until all the chlorine is removed, washing with water, drying, and distilling. The third substance is isolated from the fraction of highest boiling point (b. p. above 47° under 30 mm. pressure) of the distillation of the direct product of the action of alcohol, by allowing as much of it as possible to evaporate at the ordinary temperature under a pressure of 7—8 mm.; the residue is the nearly pure ether.

A criticism of Litterscheid's results (Abstr., 1901, i, 443) is appended. W. A. D.

Aldehyde Derivatives containing Chlorine (Carbonylchloroaldehydes). Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 121223).—*αβββ-Tetrachloroethyl chlorocarbonate*, $CCl_3\cdot CHCl\cdot O\cdot COCl$, resulting from the interaction of carbonyl choride (1 mol.) and chloral (1 mol.) in benzene solution in the presence of dimethylaniline, is a colourless oil having a disagreeable, pungent odour and boiling at 79—80° under 16 mm. pressure. When the reaction occurs between 2 mols. of chloral and 1 mol. of carbonyl chloride or the equivalent amount of trichloromethyl chloroformate or hexachlorodimethyl carbonate also in the presence of a tertiary base, dichloralchlorocarbonyl [di-αβββ-tetrachloroethyl chlorocarbonate], $CO(O\cdot CHCl\cdot CCl_3)_2$, is produced and separates as a crystalline mass melting at 64° and boiling at 170° under 11 mm. pressure. This product is almost insoluble in water but readily dissolves in the ordinary organic solvents; it is tasteless, but has a slight odour of chloral.

Benzaldehyde reacts with 1 and 2 mols. of carbonyl chloride dissolved in benzene containing quinoline, giving rise to the *α-chlorobenzyl chlorocarbonate*, $CHPhCl\cdot O\cdot COCl$, and *α-chlorobenzyl carbonate*,

$$CO(O\cdot CHPhCl)_2,$$

respectively; the former is an oil decomposing, when distilled under 1 mm. pressure, into benzylidene dichloride and carbon dioxide, the latter crystallises from light petroleum in rhombic prisms and melts at 105°. *α-Chlorobenzyl αβββ-tetrachloroethyl carbonate*,

$$CCl_3\cdot CHCl\cdot O\cdot CO\cdot O\cdot CHPhCl,$$

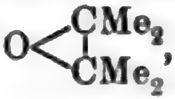
obtained either by condensing chloral with α-chlorobenzyl chlorocarbonate, or benzaldehyde with αβββ-tetrachloroethyl chlorocarbonate, crystallises from light petroleum in lustrous leaflets and melts at 81·5°; it is also produced by treating a mixture of chloral and benzaldehyde with carbonyl chloride or hexachlorodimethyl carbonate in benzene containing quinoline.

These condensations all require the presence of a tertiary base, but the bases of the pyridine series are not suitable for the purpose (compare Abstr., 1901, i, 697). G. T. M.

Nitrogen Acids. By Angelo Angeli (*Atti Real. Accad. Lincei*, 1901, [v], 10, ii, 158—161).—Nitrohydroxylaminic acid, $OH\cdot N\colon NO_2H$. may be regarded either as an oxidation product of hyponitrous acid, $OH\cdot N\colon N\cdot OH$, or as a reduction product of nitrous acid, which, however, only in exceptional cases acts as if it had the bimolecular formula.

Besides nitrohydroxylaminic acid, both hydroxylaminesulphonic and benzenesulphonehydroxamic acids are capable of yielding the residue $\colon N\cdot OH$, so that in presence of an aldehyde they give hydroxamic acids.

The action of $\colon N\cdot OH$ or an aldehyde may be one of simple addition or the residue may first combine with 1 mol. of water, forming $HN(OH)_2$, which with the aldehyde yields the additive product $OH\cdot RCH\cdot N(OH)_2$, this then being resolved into the hydroxamic acid and water. In the case of aldehydes, the formation of such intermediate additive products has not been established, but in the action of the group $:N{\cdot}OH$ on nitrosobenzene to form nitrosophenylhydroxylamine, it is extremely probable that the product $OH{\cdot}NPh{\cdot}N(OH)_2$ is first formed. The hydrate, $NH(OH)_2$, would correspond with hypophosphorous acid which forms well-defined additive products with aldehydes. T. H. P.

Researches on the Isomerisation of Pinacone and its Derivatives. By Maurice Delacre (*Compt. rend.*, 1901, **133**, 738—740. Compare Abstr., 1896, i, 591, 662).—Neither of the formulæ, $CMe_3{\cdot}COMe$ and  $O{<}\begin{array}{l}CMe_2\\ |\\ CMe_2\end{array}$, proposed for pinacolin (methyl *tert.*butyl ketone) appear to represent completely the reactions of the compound. The author thinks that free pinacolin is a mixture of the two forms in a state of equilibrium. This view is based on the following reactions. With pinacolin, phosphorus pentachloride gives a liquid chloride, $CMe_3{\cdot}CCl{:}CH_2$, and the solid chlorides, (*a*) $CMe_3{\cdot}CMeCl_2$, from which an acetylene hydrocarbon is obtainable; (*b*) $CMe_3{\cdot}CCl_2{\cdot}CH_2Cl$, which is formed by the action of phosphorus pentachloride on the liquid chloride; (*c*) $CClMe_2{\cdot}CClMe_2$(?), which yields, with alcoholic potassium hydroxide, tetramethylethylene. With moist pinacolin, sodium gives symmetrical reduction products.

Pinacolyl alcohol yields a bromide which is identical with the compound obtained from hydrogen bromide and tetramethylethylene. The liquid chloride above mentioned yields on reduction a *hydrocarbon*, $CMe_3{\cdot}CH{:}CH_2$, boiling at 44°, which, with hydrogen bromide, forms an additive product isomeric with pinacolyl bromide; it reacts with moist silver oxide, producing mainly a secondary *alcohol*,

$$CMe_3{\cdot}CHMe{\cdot}OH,$$

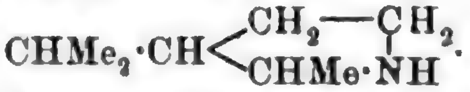
whilst with dilute potassium hydroxide, tetramethylethylene is formed. Pinacolyl bromide, on the other hand, with any moist oxide, gives, at 80—100°, mainly tetramethylethylene, together with a small quantity of the secondary alcohol.

Oxidation of pinacolin yields 50 to 60 per cent. of trimethylacetic acid and acetone (?).

The hydrocarbon to which Couturier (Abstr., 1893, i, 244) ascribes the formula $CMe_3{\cdot}CH{:}CH_2$, is regarded by the author as having the formula $CMe_2{\cdot}CH{\cdot}CMe{:}CH_2$, as the chloride formed from it and hydrogen chloride is identical with pinacolyl chloride.

The formula $OH{\cdot}CMe_2{\cdot}CMe{:}CH_2$ is given to the compound formed in the action of potassium hydroxide on the additive product of hypochlorous acid and tetramethylethylene. K. J. P. O.

Terpenes and Ethereal Oils. By Otto Wallach (*Annalen*, 1901, **319**, 77—120).—[With Ad. Gilbert.]—The base, $C_8H_{13}N$, produced by treating methylheptenoneoxime with phosphoric oxide (compare Abstr., 1900, i, 46), may contain either a pyridine or a pyrroline nucleus, and accordingly the *base*, $C_8H_{17}N$, obtained by reducing this tertiary amine with sodium and alcohol, is either a trimethylpiperidine,

$CMe_2\Big<\begin{matrix}CH_2-CH_2\\ NH\cdot CHMe\end{matrix}\Big>CH_2$, or $CMe_2\Big<\begin{matrix}CH_2-CH_2\\ CHMe\cdot NH\end{matrix}\Big>CH_2$, or a trimethylpyrrolidine, $CHMe_2\cdot CH\Big<\begin{matrix}CH_2\cdot CH_2\\ \vert\\ NH-CHMe\end{matrix}$, or  $CHMe_2\cdot CH\Big<\begin{matrix}CH_2-CH_2\\ \vert\\ CHMe\cdot NH\end{matrix}$.

The physical properties of the new base favour the view that it is a piperidine derivative. It is a colourless oil, having an odour like that of piperidine and boiling at 166°; the sp. gr. is 0·859 at 19° and n_D 1·4596. The hydrochloride is syrupy, the *platinichloride* crystallises in needles melting at 173°, the *aurichloride* melts at 118°. The new base is a secondary amine isomeric with coniine. With nitrous acid, it yields an oily *nitrosoamine* boiling at 134° under 18 mm. pressure, and when converted into the cyanamide, $C_6H_{16}N\cdot CN$, it gives rise to two *thiocarbamides* by the action of ammonium sulphide (compare Abstr., 1899, i, 658), one forming plates melting at 171°, the other crystallising in woolly needles and melting at 154—155°. When treated with excess of methyl iodide in methyl alcohol, the amine gives rise to two *quaternary iodides*, $C_8H_{16}NMe_2I$, which are separated by the difference of their solubilities in alcohol. The α-compound is only slightly soluble in alcohol or water, and melts at 238°; the corresponding *aurichloride*, $C_8H_{16}NMe_2AuCl_4$, melts at 105°. The β-compound, produced in larger amount, crystallises in needles and melts at 159—160°; it is readily soluble in water or alcohol; the corresponding aurichloride melts at 99°. These quaternary iodides yield isomeric tertiary bases when their hydroxides are distilled in a vacuum.

The tertiary *amine*, $C_8H_{15}{:}NMe$, derived from the α-iodide boils at 167—169° and yields a quaternary *iodide*, crystallising in lustrous scales and melting at 231°.

The isomeric tertiary *amine* produced from the β-iodide boils at 171—173°. The quaternary *iodide* prepared from this base is not homogeneous, and is obtained as a mixture of plates melting at 217°, and needles melting at 201°.

The iodides of the tertiary bases yield hydroxides, which, on distillation in a vacuum, give rise to a mixture of trimethylamine and unsaturated hydrocarbon. The *hydrocarbon*, C_8H_{14}, from the β compound, boils at 107—110° and is isomeric with conylene.

[With A. Blembel.]—*Bromomethylheptenone*,

$CMe_2{:}CBr\cdot CH_2\cdot CH_2\cdot COMe$,

produced by adding bromine to a methyl alcohol solution of methylheptenoneoxime and pouring the mixture into a 10 per cent. solution of sodium hydroxide, is isolated in the form of its *semicarbazone*, $C_8H_{13}Br{:}N\cdot NH\cdot CO\cdot NH_2$, a substance crystallising from alcohol in white leaflets and melting at 184°. The ketone itself, obtained from the semicarbazone by hydrolysis with 50 per cent. sulphuric acid, boils at 96° under 9 mm. pressure, and has a sp. gr. 1·2715 at 20° and n_D 1·4913. The *oxime*, $C_8H_{13}Br{:}NOH$, melts at 58° and boils at 140° under 9 mm. pressure; it is exceedingly soluble in the ordinary organic solvents. The *benzylidene* compound, $C_8H_{11}OBr{:}CHPh$, formed from its generators, dissolved in alcohol containing a small amount of sodium hydroxide, crystallises in lustrous, white leaflets and melts at 155°.

The bromo-ketone, when treated with sodium hypobromite, yields *γ-bromo-δ-methyl-γ-hexenoic acid*, $CMe_2\colon CBr\cdot CH_2\cdot CH_2\cdot CO_2H$, and this substance, on treatment with bromine, gives *γγδ-tribromo-δ-methylhexoic acid*, $CMe_2Br\cdot CBr_2\cdot CH_2\cdot CH_2\cdot CO_2H$, which separates from alcohol in crystals melting at 161°.

The bromo-ketone is reduced to methylheptenone by sodium and alcohol, whilst the oxime, under these conditions, yields methylheptenylamine.

Lævulic acid is obtained by oxidising the bromo-ketone, first with potassium permanganate, and then with chromic acid.

The semicarbazone, or a solution of its generators, when heated for some time with dilute sulphuric acid, yields a mixture containing two bases, one having the formula $C_8H_{11}N$, which is identified as 4-amino-1 : 3-xylene, whilst the other, having the composition expressed by $C_8H_{14}N_2$, is probably a hydrazine derivative; the latter base boils at 175° under 15 mm. pressure and evolves ammonia when distilled under the ordinary pressure. These bases are also formed on boiling the bromo-ketone with hydrazine sulphate. The production of the xylidine base is evidence in favour of the constitution indicated for the bromomethylheptenone.

[With HEINRICH MEYER and E. MITTELSTENSCHEID.]—The unsaturated base, $C_8H_{15}N$, obtained by adding bromine to methylheptenylamine hydrochloride, evaporating down the aqueous solution of the additive compound and setting free the amine with an alkali hydroxide, possesses many exceptional properties. It forms, with benzaldehyde, an additive *compound* having the composition $C_{15}H_{21}ON$ and melting at 99—100°.

The *compound*, $C_{15}H_{22}O_2N$, produced by the Schotten-Baumann reaction, is a benzoyl derivative of the unsaturated base, *plus* the elements of a mol. of water.

The *base*, $C_8H_{14}NMe$, obtained in the form of its iodide by mixing together methyl iodide and the unsaturated amine at 0°, boils at 164—166° and has a sp. gr. 0·852, n_D 1·4663 at 20°, mol. refraction 45·21 (calculated 45·08). The *iodide* crystallises from alcohol and ether in colourless needles melting at 200—205°; the *picrate* and *platinichloride* melt respectively at 84—85° and 194—195°. The monomethyl derivative is not acted on by nitrous acid and therefore seems to be a tertiary base.

Further methylation of the tertiary amine and treatment of the product with moist silver oxide results in the formation of trimethylamine and a ketone, $C_8H_{14}O$.

This ketone, a new *methylheptenone*, is more readily prepared by treating the unsaturated base, $C_8H_{15}N$, with nitrous acid; it boils at 161—162°, and has a sp. gr. 0·842 and n_D 1·43096 at 20°, the found and calculated values for the mol. refraction being 38·73 and 38·72 respectively. Its *semicarbazone* melts at 93—95°, and its *oxime* boils at 99° under 12 mm. pressure.

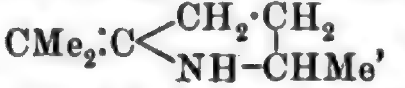
Methylheptenol, $C_8H_{15}\cdot OH$, produced by reducing the new ketone with sodium and moist ether, boils at 166—167°; it is accompanied by a syrupy product of high boiling point, which is probably a pinacone.

This alcohol differs from that obtained from natural methylheptenone in being unaffected by boiling dilute sulphuric acid.

Methylheptenylamine, $C_8H_{15}\cdot NH_2$, produced from the preceding oxime, boils at 156—158°; its *oxalate*, *hydrochloride*, *platinichloride*, and *carbamide* melt at 153—154°, 207—209°, 146—147°, and 123° respectively.

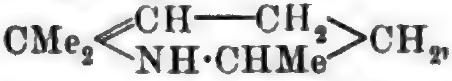
The new methylheptenone, on oxidation with potassium permanganate and chromic acid, yields a mixture of *iso*butyric and oxalic acids.

The following formulæ, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}NH$,



$$CMe_2{:}C\lt\begin{array}{l}CH_2\cdot CH_2\\ NH-CHMe\end{array},$$

and



$$CMe_2\lt\begin{array}{l}CH\text{——}CH_2\\ NH\cdot CHMe\end{array}\gt CH_2,$$

are discussed in connection with the unsaturated base, $C_8H_{15}N$.

A ketone formed from a base having the second formula would have a constitution corresponding with $CHMe{:}CH\cdot CH_2\cdot CO\cdot CHMe_2$, and this substance would, on oxidation, yield *iso*butyric acid.

Further investigations, however, are required in order to explain fully the constitutions of the compounds described in the last section of this communication. G. T. M.

Condensation Reactions of Diketones. By THEODOR POSNER (*Ber.*, 1901, **34**, 3973—3986. Compare Abstr., 1901, i, 14 and 703).—α-Diketones can react with 2 mols. of hydroxylamine, phenylhydrazine, or semicarbazide, and different substituents do not hinder the condensation, as is the case with mercaptans. β-Diketones react with semicarbazide (1 mol.), yielding pyrazole derivatives.

Diacetyldisemicarbazone, $C_2Me_2(N\cdot NH\cdot CO\cdot NH_2)_2$, crystallises from acetic acid in small plates melting at 278—279° and is insoluble in most solvents. *Diacetylphenylhydrazone-semicarbazone*,

$$N_2HPh{:}CMe\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

crystallises in yellow needles melting at 229—230° and is insoluble in water or ether.

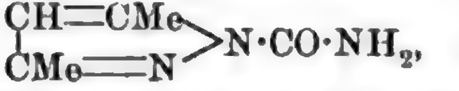
Acetylpropionyldisemicarbazone,

$$NH_2\cdot CO\cdot N_2H{:}CMe\cdot CEt{:}N_2H\cdot CO\cdot NH_2,$$

crystallises in needles melting at 251—252°; attempts to prepare the monosemicarbazone were unsuccessful.

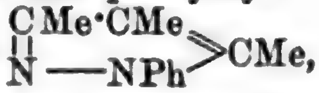
The *phenylhydrazone-semicarbazone*, $N_2HPh{:}CMe\cdot CEt{:}N_2H\cdot CO\cdot NH_2$, melts at 199—200°.

Benzil and semicarbazide react only when their alcoholic solution is warmed, and the product is a mixture of *α-benzilmonosemicarbazone*, crystallising in yellow needles and melting at 164—165° with the stereoisomeric *β-compound* melting at 221°; when the mixture is heated for several hours, the β-isomeride only is formed, but when warmed at 60° for half-an-hour, the α-compound is the chief product.

3 : 5-*Dimethylpyrazole*-1-*carboxylamide*,  $\begin{array}{l}CH{=}CMe\\ CMe{=}N\end{array}\gt N\cdot CO\cdot NH_2$, is obtained by the action of an aqueous solution of semicarbazide hydrochloride, and sodium acetate on an alcoholic solution of acetylacetone. It sinters at 109°, is completely melted at 111·4—112·4°, and dissolves in hot water, alcohol, or ether. On treatment with ammoniacal silver

nitrate, it yields the silver derivative of 3 : 5-dimethylpyrazole (Rothenburg, Abstr., 1894, i, 384).

3 : 4 : 5-*Trimethylpyrazole*-1-*carboxylamide*, obtained from methylacetylacetone, crystallises in needles melting at 148—149°, and on treatment with ammoniacal silver nitrate yields the silver derivative of 3 : 4 : 5-trimethylpyrazole. Methylacetylacetone and phenylhydrazine acetate yield 1-*phenyl*-3 : 4 : 5-*trimethylpyrazole*,



$\begin{array}{l}\text{CMe}\cdot\text{CMe}\\ \|\\ \text{N}\text{——}\text{NPh}\end{array}\!\!>\text{CMe}$,

in the form of an oil boiling at 278—280° under 768 mm. pressure; the *hydrochloride* melts at 52—53°, and the *picrate* at 100—103°.

3-*Phenyl*-5-*methylpyrazole*-1-*carboxylamide*, obtained from benzoylacetone and semicarbazide, crystallises in small needles melting at 154—156°. Benzoylacetophenone and semicarbazide react only slowly and require vigorous boiling in aqueous alcoholic solution for 4 hours. The product is Knorr and Duden's 3 : 5-diphenylpyrazole (Abstr., 1893, i, 231). Benzoylacetophenone and hydroxylamine yield diphenyl*iso*oxazole (Abstr., 1896, i, 189).

Acetonylacetonedisemicarbazone, $C_2H_4(CMe{:}N_2H{\cdot}CO{\cdot}NH_2)_2$, melts at 223—224° and is insoluble in most solvents with the exception of boiling water.

Dimethylacetonylacetone phenylhydrazone,

$$CHMe_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}N_2HPh,$$

crystallises in brownish-red needles melting at 55—57°; the corresponding *semicarbazone*, $CHMe_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}N_2H{\cdot}CO{\cdot}NH_2$, melts at 201°. The diphenylhydrazone and disemicarbazone could not be obtained. J. J. S.

Carbamide Derivatives of Sugars. II. By N. Schoorl (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, **4**, 214—217).—A detailed account of the physical and chemical properties of dextrose-ureide previously described (Abstr., 1901, i, 258). It has a sp. gr. 1·48 at 25° and the heat of combustion is 8307 *K* per gram-molecule. The ureide does not reduce a slightly acid solution of copper acetate, is only slowly oxidised at the ordinary temperature by hypobromites, but is quickly decomposed by nitrous acid at 0°. Its aqueous solution is only slightly hydrolysed by alkalis, but the rotatory power undergoes a rapid change. When acetylated in the presence of zinc chloride, the ureide yields a crystalline *pentacetyl* derivative melting at 200°, and, when benzoylated, a *tetrabenzoyl* derivative melting at 117°. The following substituted carbamides have been found to change the rotation of a solution of dextrose in dilute sulphuric acid: methyl-, phenyl-, and benzyl-carbamides, *as*-dimethylcarbamide, thiocarbamide, biuret, and urethane.

The only sugars which condense with carbamide are those which contain an open carbonyl group, such as the aldopentoses and aldohexoses and of the bihexoses, lactose and maltose. R. H. P.

Optical Rotatory Power of Sucrose dissolved in Pyridine. By Guy Maurice Wilcox (*J. Physical Chem.*, 1901, **5**, 587—599).—The specific rotation of sucrose in pyridine solution at 25° decreases from 86·7 for a 1 per cent. solution to 83·6 for a 6·25 per cent. solution, the curve being approximately a straight line. Substitution of water for pyridine causes a considerable decrease in the rotation and a minimum value of 66·0 was obtained when the percentage of water reached 80, the value in pure water being 66·6. The effect of temperature was investigated between − 10° and 105°; the specific rotation decreased from 88·7 to 77·0 between these limits, the rate of increase being slightly greater at low than at high temperatures, whilst the temperature coefficient is throughout considerably greater than in aqueous solution, a result probably due to the greater expansion of the pyridine. The molecular weight as determined by the boiling point gave results lower than the theoretical and increasing with concentration. L. M. J.

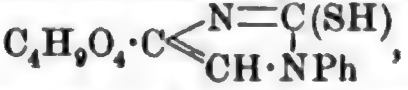
Inversion of Sucrose. By EDMUND O. VON LIPPMANN (*Ber.*, 1901, **34**, 3747—3750).—A criticism of recent theories of sugar inversion (compare Abstr., 1901, ii, 89). T. M. L.

Detection of Chitosamine [Glucosamine]. By CARL NEUBERG and H. WOLFF (*Ber.*, 1901, **34**, 3840—3846).—*Glucosamine hydrochloride* p-*nitrophenylhydrazone*,

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_3{\cdot}CH(NH_2,HCl){\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

forms microscopic needles melting and decomposing at 210° and dissolves in water, yielding a pale yellow solution which turns deep red on the addition of fixed alkalis. The corresponding *hydrobromide* begins to decompose at 190°.

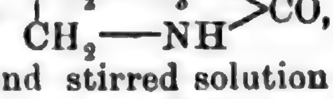
A-Tetrahydroxybutyl-1-phenyliminoazolyl-2-mercaptan,



$$C_4H_9O_4{\cdot}C{<}\begin{matrix}N{=}C(SH)\\ CH{\cdot}NPh\end{matrix},$$

obtained from glucosamine and phenylthiocarbimide, forms long, colourless prisms melting at 208° and has $[\alpha]_D$ +58°20′; it yields precipitates with silver nitrate, copper sulphate, or mercuric chloride solution. The corresponding 1-*allyl* derivative melts at 138°.

None of the compounds described above is of use in the identification of glucosamine, as, although readily obtained from the pure base, they cannot be obtained in a crystalline form from mixtures containing other bases. The best method of identification is the conversion into nor*iso*saccharic acid (Fischer and Tiemann, Abstr., 1894, i, 167), the alkaloidal salts of which are characteristic. The *cinchonine* salt of this acid crystallises in elastic needles containing $2H_2O$ and melting at 208°, it is soluble in hot water, but only sparingly so in cold, is insoluble in acetone, chloroform, ethyl acetate, or benzene, and has $[\alpha]_D$ − 175°. The *quinine* salt melts at 207° and has $[\alpha]_D$ − 125° and the *brucine* salt melts at 199°. J. J. S.

Ethylenediamine Carbonate. CHEMISCHE FABRIK AUF ACTIEN (E. SCHERING) (D.R.-P. 123138).—The *substance*,  $\begin{matrix}CH_2{\cdot}NH_3{\cdot}O\\ CH_2{-\!\!-}NH\end{matrix}{>}CO$, obtained by passing carbon dioxide into a cooled and stirred solution of ethylenediamine, is a crystalline substance vaporising at 170°; it is stable on exposure, its solution has an alkaline reaction and taste, and when evaporated leaves a syrupy residue. G. T. M.

Discrimination between Basic and Acidic Functions in Solutions of Amino-acids by means of Formaldehyde. By HUGO SCHIFF (*Annalen*, 1901, **319**, 59—76. Compare Abstr., 1899, i, 870).—Glycine is appreciably acid to phenolphthalein, but requires only about half the calculated amount of potassium hydroxide to produce neutrality; in the presence of formaldehyde, however, it behaves as a monobasic acid, but even in this case the quantity of alkali required diminishes as the solution is diluted. Phenylglycine, owing to the acidic character of the phenyl group, behaves in solution as a monobasic acid, even without the addition of formaldehyde; the three aminobenzoic acids exhibit a similar behaviour.

α-Alanine itself is only feebly acid towards phenolphthalein, and even in a concentrated solution of formaldehyde it requires less than 1 mol. of potassium hydroxide to give the neutral reaction.

Methylene-α-alanine, a white, amorphous, soluble substance, behaves as a monobasic acid in concentrated solutions; it yields the *copper* salt, $(CH_2:N\cdot C_2H_4\cdot CO_2)_2Cu,2H_2O$. Taurine is slightly acid in concentrated, and neutral in dilute, solutions, but behaves as a monobasic acid in the presence of the aldehyde, even when the dilution is considerable.

Leucine and tyrosine in strong solutions of the aldehyde behave as monobasic acids, but the action of this reagent is rendered incomplete on dilution. Methyleneasparagine reacts as a monobasic acid. Aspartic acid does not yield a methylene compound nor is its basicity appreciably affected by the aldehyde. Its sodium salt, however, becomes distinctly acid when treated with formaldehyde, the amount of potassium hydroxide required to neutralise the second carboxyl group being 75—80 per cent. of the theoretical; the action of the aldehyde diminishes rapidly as the solution is diluted.

Since neutral asparagine is changed into monobasic aspartic acid by the conversion of the radicle $-CO\cdot NH_2$ into carboxyl, it follows that the sodium salt is $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CO_2Na$, the acid function of the second carboxyl being neutralised by the adjacent amino-group.

Tetraspartic acid itself is tetrabasic, but the fifth carboxyl group is indicated under the influence of the aldehyde, 4·8 mols. of potassium hydroxide being required to neutralise 1 mol. of the acid in the presence of this reagent.

These changes in basicity are reversible and are affected by the mass of the reagents, the results obtained varying with the relative proportions of formaldehyde and water.

On adding formaldehyde to aqueous solutions of ammonium salts, neutral hexamethylenetetramine is produced, and the combined acid set free can be titrated with standard alkali solutions. On the other hand, formaldehyde can be estimated alkalimetrically by adding to its solution excess of ammonium chloride. Boric acid and other weak acids are readily liberated from their ammonium salts by treating these compounds with formaldehyde solution. G. T. M.

Resolution of Racemic Amino acids. V. By EMIL FISCHER and RUDOLF HAGENBACH (*Ber.*, 1901, **34**, 3764—3767. Compare Abstr., 1900, i, 172, 646, 647).—l-*Benzoyl*-d-*amino*-n-*hexoic acid*,

$C_{13}H_{17}O_3N$, isolated from the racemic acid by means of the cinchonine salt, crystallises from hot water with long, colourless needles with $\frac{1}{2}H_2O$, melts at 53° (corr.), and has $[\alpha]_D$ $-21·9°$ in water at 20°. The l-*aminohexoic acid* prepared from this has $[\alpha]_D$ $-22·4°$; Schulze and Likiernik obtained by fermentation an acid which had $[\alpha]_D$ $-26·5°$ (Abstr., 1893, i, 309).

d-*Benzoyl-a-amino*-n-*hexoic acid* has $[\alpha]_D$ $+21·4°$. d-*Aminohexoic acid* has $[\alpha]_D$ $+21·3°$. T. M. L.

Derivatives of the Alkali Metals and Cyclic Aminoketones.

By Emanuel Merck (D.R.-P. 121505. Compare Abstr., 1901, i, 670). —Tropinone, vinyldiacetoneamine, and triacetoneamine, when dissolved in dry ether and treated with sodium ethoxide or methoxide, either solid or dissolved in absolute alcohol, yield yellowish-white precipitates consisting of the respective sodium derivatives. The potassium derivatives are produced from potassium ethoxide in a similar manner. G. T. M.

Formation of Carbamide by the Oxidation of Physiological Nitrogenous Substances by means of Permanganate in Acid Solution.

By Adolf Jolles (*Ber.*, 1901, **34**, 3786—3787).—In opposition to Falta (Abstr., 1901, i, 795), the author finds that uric acid in a 0·02 per cent. aqueous solution containing 1 per cent. of sulphuric acid gives a quantitative yield of carbamide, but not the slightest trace of ammonia when oxidised with a slight excess of permanganate added gradually to the boiling solution. G. T. M.

Crystallography of some Derivatives of Carbamide.

By G. Mez (*Zeit. Kryst. Min.*, 1901, **35**, 242—271).—The results are given of detailed determinations of the crystallographic and other physical characters of carbamide and of sixteen of its derivatives. The relations between the angular elements and between the topic axial ratios, depending on the introduction of different radicles, are discussed. L. J. S.

Primary Arsines.

By Arthur W. Palmer and William M. Dehn (*Ber.*, 1901, **34**, 3594—3599).—*Methylarsine*, AsH_2Me, is formed by the reduction of methyldichloroarsine, $AsMeCl_2$, but is best prepared by acting on an alcoholic suspension of sodium methylarsenate and amalgamated zinc dust with hydrochloric acid in an atmosphere of dry hydrogen in an apparatus entirely made of glass. The gas evolved is passed through water, dried over soda-lime, and liquefied by solid carbon dioxide. It is a colourless, readily mobile liquid which boils at 2° under 755 mm. pressure, and at 17° under 1·5 atmospheres pressure. It has the penetrating, repulsive odour of cacodyl and fumes in the air, but is not spontaneously inflammable. If air has access to the apparatus in which it is prepared, the arsine is oxidised to a lustrous, red substance, the nature of which is not known. When pure, dry oxygen is added to gaseous methylarsine over mercury, equal volumes of the two gases combine, forming water and methylarsine oxide, AsMeO, which then slowly combines with oxygen forming methylarsenic acid.

On one occasion, the addition of the oxygen was followed by a mild explosion, and the whole of the arsenic was deposited in the free state. The arsine is oxidised by concentrated nitric acid to arsenious acid and monomethylarsinic acid, and when passed into an alcoholic solution of iodine yields arsinmethyl iodide.

Monophenylarsine, AsH_2Ph, is prepared by a similar reaction from calcium monophenylarsenate, although La Coste and Michaelis were unable to obtain it in this way (*Annalen*, **201**, 203, 209). It is a transparent, strongly refractive oil, which boils at 148°, and smells, when concentrated, like phenylcarbamine, when dilute, like hyacinths. In the air, it is converted into a yellow substance, which melts at 195—208° and is probably arsenobenzene. Nitric acid converts the arsine into monophenylarsinic acid and a yellow oil of unknown nature. A. H.

Simultaneous Formation of Isomeric Substitution Derivatives of Benzene. VI. Nitration of Iodobenzene.

By ARNOLD F. HOLLEMAN and B. R. DE BRUYN (*Rec. Trav. Chim.*, 1901, [ii], **20**, 352—359. Compare Abstr., 1900, i, 387, 638; 1901, i, 318).—The proportion of *o*- and *p*-iodonitrobenzenes in the product of nitration of iodobenzene was determined by the method of melting points and of sp. gr. (*loc. cit.*). The product obtained by adding gradually 25 grams of iodobenzene to a mixture of 50 c.c. of nitric acid of sp. gr. 1·48 with 10 c.c. of acid of sp. gr. 1·52 consists at −30° of 35·3 per cent. of *o*- and 64·7 per cent. of *p*-iodonitrobenzene, and at 0° of 34·2 per cent. of *o*- and 67·8 of *p*-compound.

Pure *o*-iodonitrobenzene, obtained from pure *o*-nitroaniline, has a sp. gr. 1·8100 at 155°/4° and melts at 54°; it is difficult to purify the *o*-compound obtained by the nitration of iodobenzene, and Körner, in giving the melting point as 49·4°, had not obtained the pure substance. *m*- and *p*-Iodonitrobenzenes have respectively sp. grs. 1·8039 and 1·8090 at 155°/4°.

The eutectic point of a mixture of *o*- and *p*-iodonitrobenzenes is 45·2°; the product of nitration at 30° gave a value for this constant of 43·5°, and at 0° a value 43·1°. The depression is due to the presence of about 1·1 and 1·3 per cent. of dinitroiodobenzene in the two cases; as the latter is formed only from *o*-iodonitrobenzene under the given conditions, it can be expressed as such, and the values just given for the proportions of *o*- and *p*-compounds are corrected on this basis. W. A. D.

Velocity of Substitution of a Halogen by an Alkoxyl Group in some Aromatic Halogen Nitro-compounds.

By P. K. LULOFFS (*Rec. Trav. Chim.*, 1901, **20**, 292—327. Compare Steger, Abstr., 1899, i, 745).—The method of procedure adopted was the same as that of Steger (*loc. cit.*), the special points studied being the interaction of 1-chloro- and 1-bromo-2 : 4-dinitrobenzenes with sodium methoxide and ethoxide, and of 1-iodo-2 : 4-dinitrobenzene and several other nitro-compounds with sodium ethoxide. The influence of the concentration of the alcoholic solution, the addition of water to the alcohol, the presence of a salt of sodium, and the temperature on the velocity constant, k, of the equation $-dc/dt = kc^2$, was determined; the results are given in the form of tables and curves, and in the following *résumé*.

The transformation of the monohalogen dinitrobenzenes [X : $(NO_2)_2$ =

1 : 2 : 4] by an alkyloxide takes place in only one direction, the halogen in position 1 being substituted quantitatively by the alkoxyl group; the velocity of replacement by ethoxyl is greater than that by methoxyl, and the substitution of chlorine easier than that of bromine, and much easier than that of iodine. Thus, for sodium ethoxide in an absolute alcoholic solution containing three-fifths of the gaseous concentration of the halogen dinitrobenzene at 15°, the values of *k* for chlorine, bromine, and iodine were 3·26, 2·04, and 0·455, and the times in which the reaction was one-half complete, 17·7, 35, and 128 minutes respectively. Iodine is thus much more firmly attached to the aromatic nucleus than bromine, and bromine than chlorine.

By comparison with Steger's results, it appears that the replacement of a nitro-group in *o*- or *p*-dinitrobenzene, occurs much more slowly than that of the chlorine atom in chloro-2 : 4-dinitrobenzene. Contrary to Steger's results, diminishing the concentration increases the velocity constant; this increase is greater in the case of the chloro- than in that of the bromo-compound, and for absolute ethyl than for absolute methyl alcohol. The effect of changing the concentration is thus the same as in the case of the reaction $MeI + NaOEt = MeOEt + NaI$ (Hecht, Conrad, and Brückner, Abstr., 1890, 1046).

When the alcohols employed are diluted with water, there is a definite coefficient for each dilution, even when the quantity of water is as great as 40 per cent. The addition of water diminishes the reaction constant in the case of sodium ethoxide, and initially slightly increases that of sodium methoxide, but in the latter case subsequent diminution occurs. The influence of dilution is most marked with chlorodinitrobenzene and least with iododinitrobenzene (compare Lobry de Bruyn and Steger, Abstr., 1899, i, 745).

The addition of sodium bromide or acetate to alcoholic sodium ethoxide diminishes the velocity of interaction of the latter with 1-bromo-2 : 4-dinitrobenzene; the influence of the bromide is much the greater, and is especially notable in the cases where the alcohol is diluted with water. The temperature coefficient of the action of sodium ethoxide and 1-chloro-2 : 4-dinitrobenzene is 1·28, and for 1-bromo-2 : 4-dinitrobenzene, 1·41.

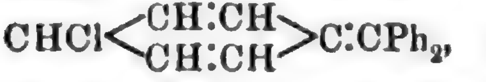
The speed of replacement of chlorine in *p*-nitrobenzyl chloride is greater than in *o*-nitrobenzyl chloride; the action of sodium ethoxide and *p*-nitrobenzonitrile does not give a definite velocity constant because both the nitro- and cyano-group undergo replacement. The action of the ethoxide on *p*- or *m*-nitrobenzoyl chloride at 0° is too rapid for measurement. W. A. D.

Molecular Weight of Nitrosoaryls. By Eugen Bamberger and Adolf Rising (*Ber.*, 1901, **34**, 3877—3880).—Nitrosobenzene, *o*- and *p*-bromonitrosobenzene, *o*- and *p*-nitrosotoluene, nitroso-*p*-xylene, and 1-nitroso-2 : 4-xylene were found to give normal values for the mol. weight, both in freezing benzene and in boiling acetone; these substances all dissolve with a bluish-green or green colour. Nitrosomesitylene gave M = 180·4 in boiling acetone and M = 233 (mean value) in freezing benzene, the calculated value being M = 149; similarly, 1-nitroso-2 : 6-xylene gave M = 188 (mean value) in boiling acetone and M = 237(mean value) in freezing benzene, the calculated value being M = 135. The indications of polymerisation to a double molecule which are thus afforded correspond closely with observations made on the colour of the solutions; both substances dissolve in the cold with an exceedingly faint bluish-green colour, which becomes darker on heating, as the colourless polymeride dissociates, and gradually becomes less intense when cooled, the polymerisation taking place only slowly. It is noteworthy that only the diortho-derivatives of nitrosobenzene are polymerised; for similar observations in the fatty series, compare Piloty (Abstr., 1898, i, 289).

The only derivative of nitrosobenzene which appears to be unimolecular in the solid state is 3 : 4-dimethylnitrosobenzene (Abstr., 1901, i, 529), which forms a clear, bluish-green solid. T. M. L.

Diphenyl Derivatives. By FRITZ ULLMANN and W. RUSSEL FORGAN (*Ber.*, 1901, **34**, 3802—3805. Compare Abstr., 1901, i, 586). —On adding a solution of *o*-nitrobenzenediazonium chloride to a cold solution of cuprous chloride, a small quantity (17 per cent.) of *o*-chloronitrobenzene is formed, together with a much larger quantity (68 per cent.) of 2 : 2′-dinitrodiphenyl. By this method, 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl was obtained from 4-chloro-2-nitroaniline (yield 59 per cent.) and 2 : 2′-dinitro-4 : 4′-ditolyl from 3-nitro-*p*-toluidine (yield 88 per cent.)

5 : 5′-*Dichloro*-2 : 2′-*dinitrodiphenyl*, $C_{12}H_6Cl_2(NO_2)_2$, prepared from 3-chloro-6-nitroaniline, crystallises in pale yellowish-brown needles melting at 170°. K. J. P. O.

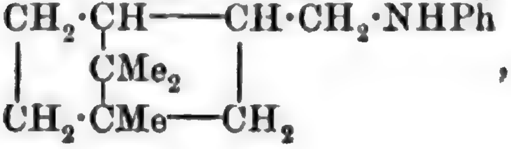
Basic Properties of Carbon and the Constitution of the so-called Triphenylmethyl. By FRIEDRICH KEHRMANN and F. WENTZEL (*Ber.*, 1901, **34**, 3815—3819. Compare Gomberg, Abstr., 1901, i, 77, 319, 638; Norris and Sanders, *ibid.*, i, 198).—Triphenylchloromethane dissolves in cold concentrated sulphuric acid, evolving hydrogen chloride and yielding a golden-yellow solution; when diluted with water, the solution remains yellow, but on further dilution becomes colourless and gives a colourless precipitate of triphenylcarbinol. Similarly, when concentrated hydrochloric acid is added to a colourless ethereal solution of triphenylcarbinol, the solution first becomes yellow and finally colourless, yielding ordinary triphenylchloromethane. The authors conclude that triphenylchloromethane and similar compounds exist in two forms, namely, CPh_3Cl, colourless, and  $CHCl<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>C{:}CPh_2$, yellow. It is from the latter that Gomberg's triphenylmethyl or rather diphenylphenylenemethane is obtained by the loss of HCl. The bivalent carbon atom would thus possess basic properties.

p-Rosaniline chloride and dichromate are both anhydrous, and are obtained from the carbinol by the loss of water. The chloride reacts with concentrated sulphuric acid, yielding a golden-yellow solution, which, on diluting with ice and water, becomes paler and finally colourless. When boiled, it turns purple, but becomes colourless again on cooling.

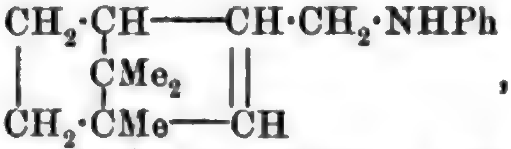
A yellow *compound*, $CPh_3Cl,SnCl_4$, is described. J. J. S.

Some Relation between Physical Constants and Constitution in Benzenoid Amines. By WILLIAM R. HODGKINSON and LEONARD LIMPACH (*Chem. News*, 1901, **84**, 221—222).—The investigations on the relationship between melting points and constitution in some amines (Proc., 1893, 41; Trans., 1901, **79**, 1080) have been continued and it is observed that the differences between the melting points of the formyl and acetyl derivatives of bases of the same constitution is constant or nearly so, moreover that this relationship is not disturbed by the replacement of a methyl group by an ethyl or methoxy-group, although, of course, the melting points of the latter compounds differ from those of the methyl compounds. Furthermore, the melting points of the formyl and acetyl derivatives of the tetramethyl bases correspond with the sum of the melting points of two xylidines less the melting point of formanilide. D. A. L.

Preparation of Hexahydrobenzylamines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 121976).—*Homocamphanylaniline*,

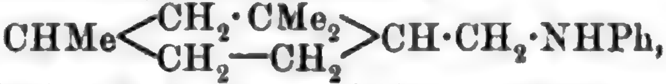


, obtained from the corresponding unsaturated amine *homocamphenylaniline*,



, or its additive product with hydrogen chloride by reduction with sodium and ethyl alcohol, is a viscid, colourless oil boiling at 220° under 20 mm. pressure.

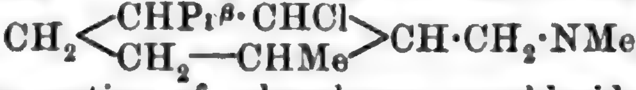
2 : 2 : 4-*Trimethylhexahydrobenzylaniline*,



$$CHMe{<}\begin{matrix}CH_2\cdot CMe_2\\ CH_2—CH_2\end{matrix}{>}CH\cdot CH_2\cdot NHPh,$$

prepared by reducing 2 : 2 : 4-trimethyltetrahydrobenzylaniline or its additive compound with hydrogen chloride, boils at 190° under 15 mm. pressure.

6-*Chloro*-2-*methyl*-5-iso*propylhexahydrobenzyldimethylamine*,



$$CH_2{<}\begin{matrix}CHPr^\beta\cdot CHCl\\ CH_2—CHMe\end{matrix}{>}CH\cdot CH_2\cdot NMe_2,$$

produced by the action of phosphorus oxychloride on 6-hydroxy-2-methyl-5-*iso*propylhexahydrobenzyldimethylamine (b. p. 140° under 14 mm. pressure), is a colourless oil, and on reduction with zinc dust and acetic acid containing a little hydrochloric acid it yields 2-*methyl*-5-iso*propylhexahydrobenzyldimethylamine*, this base being a colourless oil having an odour resembling that of coniine and boiling at 118—120° under 15—16 mm. pressure.

2-*Methyl*-5-iso*propylhexahydrobenzylaniline*, 2-*methyl*-5-iso*propylhexahydrobenzylamine*, and 2-*methyl*-5-iso*propylhexahydrobenzylethylamine*, obtained by reducing the corresponding unsaturated bases or their hydrogen chloride derivatives, are colourless oils boiling respectively at 215° (under 33 mm. pressure), and 226—228° and 135—140° under the ordinary pressure.

p-*Methylhexahydrobenzylaniline* is a colourless oil boiling at 195° under 30 mm. pressure. G. T. M.

New Bases from Anhydroformaldehydeaniline [Methyleneaniline] and its Homologues. Ernst Erdmann (D.R.-P. 121506).—Isomerides of the anhydroformaldehyde bases are produced by dissolving these substances in glacial acetic acid at temperatures below 25°, and are isolated as amorphous precipitates on diluting the products with water. The compound, $(C_7H_7N)_x$, from methyleneaniline, is a pale yellow powder having no definite melting point; it yields an *acetyl* derivative, $(C_7H_6NAc)_x$, and when reduced with zinc dust yields a mixture of aniline and *p*-toluidine in approximately equal proportion. The corresponding *o*-toluidine and *p*-xylidine compounds form white powders melting at 150° and 85—90° respectively. The *p*-toluidine and *m*-xylidine derivatives are tarry substances. These compounds dissolve in dilute hydrochloric acid, and with the substantive cotton colouring matters form lakes which are comparatively stable to acids.

G. T. M.

Preparation of Aromatic Bases [by the aid of Formaldehyde]. Ernst Erdmann (D.R.-P. 122474. Compare Troeger, Abstr., 1888, 286).—When 4-*m*-xylidine, *p*-toluidine, or *p*-chloroaniline is treated with formaldehyde solution in the presence of moderately strong hydrochloric acid, a substance is obtained possessing the property of forming lakes with the substantive cotton colouring matters, and thereby rendering these less sensitive to dilute acids. The *m*-xylidine and *p*-toluidine derivatives are yellow, amorphous substances melting respectively at 62—65° and at 65—70°. In the latter case, the crystalline base described by Troeger is obtained as a bye-product. *p*-Chloroaniline gives rise to a yellow, crystalline derivative melting at 188°, the hydrochloride of which separates from water in colourless prisms.

G. T. M.

Mono- and Di-alkylated Aromatic Amines. Badische Anilin- & Soda-Fabrik (D.R.-P. 121683. Compare Abstr., 1901, i, 695 699).—Methylnaphthionic acid (1-methylaminonaphthalene-4-sulphonic acid), $NHMe\cdot C_{10}H_6\cdot SO_3H$, obtained by heating sodium α-naphthol-4-sulphonate with a 10 per cent. solution of methylamine sulphite, $SO_3(NH_3Me)_2$, at 150° and acidifying the product, separates from solution in a crystalline form. This operation may be performed in two stages; the first consists in converting the naphtholsulphonate into its sulphurous ester by means of sodium hydrogen sulphite, and the second in treating this product with methylamine.

Sodium β-naphthol-6-sulphonate, when heated for 15 hours at 125° with an aqueous solution of methylamine and methylamine sulphite, readily yields sodium 2-methylaminonaphthalene-6-sulphonate, from which dilute acids liberate the crystalline sulphonic acid. Dimethyl-*m*-aminophenol is readily produced by treating resorcinol with a solution of dimethylamine and its sulphite at 125° and is isolated from the product in the form of its hydrochloride.

G. T. M.

Preparation of β-Naphthylamine Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 122570. Compare Abstr., 1901, i, 695, 699).—*Phenyl-β-naphthylamine-6-sulphonic acid*, produced by heating together sodium β-naphthol-6-sulphonate, aniline, and sodium hydrogen sulphite solution, is readily soluble in water and yields a bluish-violet azo-compound with diazotised *p*-nitroaniline.

2 : 5-Dihydroxynaphthalene-7-sulphonic acid, when treated in this manner, yields an amino-acid which is probably 2-*phenylamino*-5-*hydroxynaphthalene*-7-*sulphonic acid*. 2-o-*Tolylamino*-8-*hydroxynaphthalene*-6-*sulphonic acid* is obtained from 8-hydroxy-β-naphthylamine-6-sulphonic acid, *o*-toluidine, and sodium hydrogen sulphite. 2-o-*Xylylamino*-5-*hydroxynaphthalene*-7-*sulphonic acid* is produced from *o*-xylidine and 5-hydroxy-β-naphthylamine-7-sulphonic acid. Similar substituted β-naphthylamine derivatives are obtained from β-naphthol-6-sulphonic acid and *p*-phenylenediamine, and also from 8-hydroxy-β-naphthylamine-6-sulphonic acid and *p*-aminophenol. G. T. M.

Naphthalenoid Thiocarbamides containing Hydroxyl Groups. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 122286. Compare D.R.-P. 116201 and 116200).—*Thiocarbonyldihydroxydinaphthylaminedisulphonic acids*, $CS[NH·C_{10}H_5(OH)·SO_3H]_2$, are obtained by the action of carbon disulphide, sulphur, and sodium carbonate solution on the aminonaphthols and their sulphonic acids in which the amino- and hydroxy-radicles are present in positions other than 1 : 2 or 1 : 8 with respect to each other. G. T. M.

Preparation of Tertiary Aromatic Bases from their Alkyl Haloids. By Johannes Pinnow (*Ber.*, 1901, **34**, 3772).—A claim for priority in the use of the method for converting aromatic quaternary salts into the corresponding tertiary bases by heating with aqueous ammonia (compare Abstr., 1898, i, 184; 1899, i, 588, and Scholtz, Abstr., 1898, i, 567; 1901, i, 749). G. T. M.

Derivatives of Phenyl Ether. II. By Alfred N. Cook (*J. Amer. Chem. Soc.*, 1901, **23**, 806—813. Compare Abstr., 1901, i, 144).—o-*Nitrophenyl* o-*tolyl ether*, $NO_2·C_6H_4·O·C_6H_4Me$, obtained by the action of *o*-bromonitrobenzene on potassium *o*-tolyl oxide, is a dark red liquid which boils at 194—196° under 14 mm. and decomposes when heated under atmospheric pressure; it is not volatile with steam, has an oily taste, a sp. gr. 1·195 at 20°, and is soluble in the usual organic solvents. On reduction with tin and hydrochloric acid, the *hydrochloride* of o-*aminophenyl* o-*tolyl ether* is produced as a white, waxy mass; the base could not be isolated on account of its instability. By the action of sulphuric acid on *o*-nitrophenyl *o*-tolyl ether, a *sulphonic acid*, $NO_2·C_{12}H_7OMe·SO_3H$, is produced, which is a reddish-yellow, viscous liquid, soluble in 2·5 parts of water at 80°, and readily so in alcohol, benzene, or light petroleum; the *barium*, *strontium*, and *lead* salts are soluble in water to the extent of 0·745, 2, and 8·17 per cent. at 100°, and 0·12, 0·68, and 3·5 per cent. at 31° respectively.

o-*Nitrophenyl* m-*tolyl ether* is a red, oily liquid which boils at 223° under 30 mm., but decomposes if heated under atmospheric pressure; it is not volatile with steam, has a sp. gr. 1·208 at 27°, and is readily soluble in the usual organic solvents. o-*Aminophenyl* m-*tolyl ether hydrochloride* is a clear, viscous substance, readily soluble in alcohol or ether and sparingly so in water; the base is very unstable and could not be isolated. o-*Nitrophenyl*-m-*tolyl-ether-sulphonic acid* crystallises in short, yellowish-brown needles, and is soluble in water, alcohol or ether; the *barium* salt is soluble in water to the extent of 1·1 per cent. at 82° and 0·61 per cent. at 35°.

o-*Nitrophenyl*-p-*tolyl-ether-sulphonic acid* forms reddish-brown crystals, soluble to the extent of 9·8 per cent. in water at 31°, and readily soluble in alcohol, ether, benzene, or glacial acetic acid; the *barium* salt is soluble in water to the extent of 69·1 per cent. at 80° and 14·7 per cent. at 27°. E. G.

Ethoxy*iso*eugenol (Monoethoxymethylpropenylcatechol Ether). CÆSAR POMERANZ (D.R.-P. 122701. Compare Abstr., 1892, 972).—*Ethoxy*iso*eugenol* (2-*monoethoxymethyl*-4-*propenylcatechol ether*), $OEt\cdot CH_2\cdot O\cdot C_6H_3(OH)\cdot CH\colon CHMe$, results from the action of alcoholic potassium hydroxide solution on safrole at 140—150°; it is a colourless, almost odourless oil boiling at 172° under 22 mm. pressure.

G. T. M.

***iso*Chavibetol.** CÆSAR POMERANZ (D.R.-P. 123051. Compare Abstr., 1901, i, 699).—The condensation products of the alcohols with *iso*safrole having the general formula $OR\cdot CH_2\cdot O\cdot C_6H_3(OH)\cdot CH\colon CHMe$ yield *iso*chavibetol when treated with dilute alcoholic solutions of the mineral acids. G. T. M.

Substituted Thiocyanates of the *o-p*-Dinitrohydroxydiphenylamines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 122569).—1 : 3-Dithiocyano-4 : 6-dinitrobenzene, obtained by adding powdered potassium thiocyanate or the corresponding salt of another metal to an acetone solution of 1 : 3-dichloro-4 : 6-dinitrobenzene, crystallises from alcohol in pale yellow leaflets and decomposes at 185°. When this compound is treated with a mixture of sodium acetate, alcohol, and an aminophenol for 8 hours at 65°, one of the thiocyano-groups is removed and a diphenylamine derivative is produced. o-p-*Dinitro*-m-*thiocyano*-p-*hydroxydiphenylamine*,

$$SCN\cdot C_6H_2(NO_2)_2\cdot NH\cdot C_6H_4\cdot OH,$$

obtained from *p*-aminophenol, separates from acetone, alcohol, or glacial acetic acid in red crystals melting at 227—228°; the corresponding *compound* from *o*-aminophenol melts at 255°. The *sodium* salt,

$$SCN\cdot C_6H_2(NO_2)_2\cdot NH\cdot C_6H_3(OH)\cdot SO_3Na,$$

of the *p*-aminophenol-*o*-sulphonic acid *derivative* crystallises in reddish-brown needles; the aminosalicylic acid *compound* is a yellowish-brown powder; these substances decompose without melting. G. T. M.

Preparation of Chlorides and Anhydrides of the Carboxy-acids. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 123052).—When 1 mol. of an aromatic sulphonic chloride is heated with 1 mol. of the anhydrous salt of a carboxylic acid, the corresponding acid chloride is formed in accordance with the following equation: $Ph\cdot SO_2Cl + R\cdot CO_2Na = Ph\cdot SO_3Na + R\cdot COCl$. If 2 mols. of the anhydrous salt are employed, the corresponding anhydride is produced. Acetyl chloride and acetic anhydride are obtained by the action of *p*-toluenesulphonic chloride on 1 and 2 mols. of sodium acetate respectively. Propionic and benzoic anhydrides and salicylyl chloride may also be prepared by this process. G. T. M.

Phenylglycine-*o*-carboxylic Acid. Daniel Vorländer and Rudolf von Schilling (D.R.-P. 121287).—Nitroso-*o*-tolylglycine, $C_6H_4Me\cdot N(NO)\cdot CH_2\cdot CO_2H$, an oil obtained by treating *o*-tolylglycine with sodium nitrite and dilute sulphuric acid, yields nitrosophenylglycine-*o*-carboxylic acid (m. p. 120°) on treatment with potassium permanganate solution; the oxidation product when reduced with zinc dust and sodium hydroxide or sulphurous acid, or when boiled with alcoholic hydrogen chloride, gives rise to phenylglycine-*o*-carboxylic acid (compare Abstr., 1900, i, 295, and 1901, i, 462, 463).

G. T. M.

Electric Conductivity of Chloro- and Bromo-nitrobenzoic Acids. By Arnold F. Holleman and B. R. de Bruyn (*Rec. Trav. Chim.*, 1901, [ii], **20**, 360—364).—The following table gives a comparison of the affinity constants, *k*, of chloro- and bromo-nitrobenzoic acids as determined with carefully purified material and as calculated by Ostwald and Bethmann's method:

Acid.	Structure. $CO_2H : X : NO_2$.	*k* calc.	Found μ_∞.	*k* found.
Chloronitrobenzoic	1 : 2 : 5	0·75	356	0·62
,, ...	1 : 2 : 3	0·75	356	0·87
,, ...	1 : 3 : 6	1·60	356	1·42
,, ...	1 : 3 : 2	1·60	356	0·44
Bromonitrobenzoic	1 : 2 : 5	0·83	353	0·91
,, ...	1 : 2 : 3	0·83	353	1·16
,, ...	1 : 3 : 6	1·41	355	1·55
,, ...	1 : 3 : 2	1·41	353	0·34

There is a satisfactory agreement between observed and calculated values except in the case of the 1 : 3 : 2-acids. In the original paper, a table is given showing a similar comparison of a large number of other disubstituted benzoic acids, and here again satisfactory agreement is visible except in the case of α-nitrophthalic acid (calc. 12·4, found 1·22), β-resorcylic acid (calc. 1·73, found 5·0) and *o*-nitrosalicylic acid (calc. 0·58, found 1·57). In all cases where a divergence occurs, the position of the groups is adjacent. It is true that *o*-chloro- and *o*-bromo-*m*-nitrobenzoic acids and hydroxysalicylic acid $[CO_2H : (OH)_2 = 1 : 2 : 3]$ give a good agreement, but here the halogen or hydroxyl is in the ortho-position relatively to the carboxyl; when a great divergence occurs it is the nitro-group which is in this position.

W. A. D.

Anthranil. By Otto Buhlmann and Alfred Einhorn (*Ber.*, 1901, **34**, 3788—3793).—The substance obtained by Einhorn and Bull

(Abstr., 1897, i, 345) by the action of hydroxylamine hydrochloride on anthranil in alcoholic solution is shown to be the oxime of *o*-aminobenzaldehyde, and not the oxime of anthranil; the hydroxylamine has acted as a reducing agent.

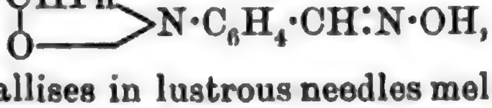
Free hydroxylamine and anthranil yield a *compound*, $C_7H_8O_2N_2$, which crystallises from benzene in white, prismatic needles melting at 114—115°, and is not the oxime of anthranil, but probably *o*-hydroxylaminobenzaldehyde; it dissolves in dilute alkalis and acids, and is quantitatively converted by the latter into anthranil. With benzaldehyde, it gives a condensation *product*, $C_{14}H_{12}O_2N_2$, which crystallises in pale yellow, prismatic needles melting and decomposing at 164°.

Hydrazine hydrate and anthranil react in the presence of alcohol at 100° to form a *compound*, $C_7H_9ON_3$, which crystallises in pale-yellow, transparent, prismatic leaflets melting and decomposing at 120°; dilute acids immediately decompose it into anthranil and a hydrazine salt.

From phenylhydrazine and anthranil a *compound*, $C_{13}H_{13}ON_3$, is obtained as yellow, prismatic needles, which darken at 140°, and melt and decompose at 155°; when boiled with acetic acid, or heated alone, it is converted into the phenylhydrazone of *o*-aminobenzaldehyde.

Other compounds, besides anthranil, which contain the group $\cdot CO\cdot NH\cdot$, are able to combine with hydrazines without elimination of water; thus when benzamide and phenylhydrazine are heated at 100° in acetic acid solution, *acetylbenzamidephenylhydrazone hydrate*, $NHPh\cdot NH\cdot CPh(NH_2)\cdot O\cdot COMe$, is formed, and crystallises from benzene in white, silky needles melting at 105°; acids decompose it into phenylhydrazine, acetic acid, and benzamide. K. J. P. O.

Constitution of Anthranil. By **Eugen Bamberger** and **Ed. Demuth** (*Ber.*, 1901, **34**, 4015—4028. Compare Buhlmann and Einhorn, preceding abstract).—When anthranil (1 mol.) and hydroxylamine, (3 mols). are heated together in solution in absolute alcohol, *o-hydroxylaminobenzaldoxime*, $OH\cdot NH\cdot C_6H_4\cdot CH{:}N\cdot OH$, is formed; this substance can also be obtained by reduction of *o*-nitrobenzaldoxime with zinc dust; it crystallises in long, white, silky needles melting at 120—121°, is soluble in alkalis with a lemon-yellow colour, and reduces silver nitrate and Fehling's solution. In dilute acids, it dissolves, and is then converted into anthranil and hydroxylamine. With aldehydes, it condenses; thus with benzaldehyde, a *benzylidene* compound,



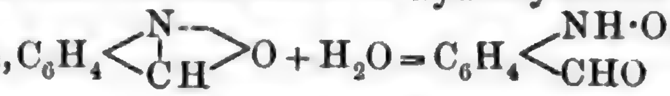
$$\begin{array}{l}\mathrm{CHPh}\\ |\\ \mathrm{O}\end{array}\!\!>\!N\cdot C_6H_4\cdot CH{:}N\cdot OH,$$

is formed which crystallises in lustrous needles melting at 172—172·5°; the p-*nitrobenzylidene* compound crystallises in small, silky needles; both substances dissolve in alkali hydroxides with an intense red coloration.

Molecular proportions of anthranil and hydroxylamine, dissolved in dilute alcohol, gave mainly *o-azoxybenzaldoxime*, $ON_2(C_6H_4\cdot CH{:}NOH)_2$, which crystallises in needles melting at 210·5—211°; this azoxy-compound was also prepared from *o*-azoxybenzaldehyde and hydroxylamine.

When 2 mols. of hydroxylamine interact with 1 mol. of anthranil, besides *o*-azoxybenzaldoxime, *o*-triazobenzaldoxime, *o*-aminobenzaldoxime, and benzaldoxime are formed. Prolonged action of a still greater excess of hydroxylamine on anthranil produces mainly *o*-aminobenzaldoxime together with the other substances just mentioned.

In the presence of potassium hydroxide, hydroxylamine and anthranil yield *o*-nitro- and *o*-amino-benzaldoxime.

The view is expressed that the first action of hydroxylamine on anthranil is one of hydration,  $C_6H_4{<}\begin{matrix}N\\|\\CH\end{matrix}{>}O + H_2O = C_6H_4{<}\begin{matrix}NH\cdot OH\\CHO\end{matrix}$. From the hydroxylaminobenzaldehyde, *o*-aminobenzaldehyde, *o*-nitrobenzaldehyde, and *o*-azoxybenzaldehyde would be produced respectively by oxidation or reduction. It is suggested that the *o*-triazobenzaldehyde is produced by union of the group $CHO\cdot C_6H_4\cdot N\colon$ (formed from anthranil) and molecular nitrogen, which arises by oxidation of the hydroxylamine (compare this vol., i, 25). In the presence of excess of hydroxylamine, these aldehydes would be converted into oximes.

K. J. P. O.

Methyl Methylanthranilate. SCHIMMEL & Co. (D.R.-P. 122568).—*Methyl methylanthranilate*, $NHMe\cdot C_6H_4\cdot CO_2Me$, prepared either by treating methylanthranilic acid with methyl alcohol and concentrated hydrochloric or sulphuric acid, or by heating sodium or potassium anthranilate with potassium hydroxide and methyl iodide under pressure, boils at 130—131° under 13 mm. pressure, and has a sp. gr. 1·120 at 15°; its solution has a blue fluorescence. This ester has the characteristic odour of mandarin oil, and is contained in this essence to the extent of 1·5 per cent.

G. T. M.

Preparation of *o*-Benzoicsulphimide ("Saccharin") and other Aromatic Sulphonamides. BASLER CHEMISCHE FABRIK (D.R.-P. 122567).—Benzene- and *o*-toluene-sulphinic acids, dissolved in a mixture of alcohol and excess of aqueous ammonia and treated with chlorine at 35—40°, yield the corresponding amides. *o*-Benzoicsulphimide ("saccharin") is obtained by this process in one operation, and from monomethyl *o*-carboxybenzenesulphinate, $SO_2H\cdot C_6H_4\cdot CO_2Me$ (m. p. 98—99°), the latter substance being produced from diazotised methyl anthranilate by the action of alcoholic sulphurous acid and copper sulphate.

G. T. M.

Stable Carbonyl Derivatives of Indigo-white. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 121866).—The normal carbonic ester of indigo-white is produced on treating a mixture of indigo-white, acetone, and sodium hydroxide solution with carbonyl chloride; it decomposes without melting, yielding indigotin, and is hydrolysed by warming with dilute solutions of the alkali hydroxides. The product of the action of methyl or ethyl chlorocarbonate on indigo-white in the presence of alkali hydroxides, when extracted with alcohol, yields an insoluble *ester* crystallising from acetone in felted needles and melting at 257—259°; the alcoholic extract contains a second *ester* separating in needles and melting at 110—112°. These esters are also obtained along with the infusible product by treating indigo-white with carbonyl chloride in aqueous sodium hydroxide solution.

G. T. M.

Phenanthrene Derivatives. By ROBERT PSCHORR (*Ber.*, 1901, **34**, 3998—4007).—[With C. SEYDEL.]—The hitherto unknown

2-methoxyphenanthrene was synthesised by condensing 6-nitro-3-methoxybenzaldehyde with sodium phenylacetate in the presence of acetic anhydride at 100°; the *a-phenyl-β-6-nitro-3-methoxycinnamic acid*, $NO_2\cdot C_6H_3(OMe)\cdot CH{:}CPh\cdot CO_2H$, thus obtained crystallises in pale yellow leaflets melting at 165—166°, and yields sparingly soluble silver, lead, and calcium salts, which all crystallise in needles.

a-Phenyl-β-3-methoxy-6-aminocinnamic acid,

$$NH_2\cdot C_6H_3(OMe)\cdot CH{:}CPh\cdot CO_2H,$$

obtained by reducing the corresponding nitro-compound with ferrous sulphate in presence of ammonia, crystallises in greyish-violet leaflets having a silvery lustre, which become coloured at 182—187° and melt at 227—228°; this substance forms well-crystallised salts both with acids and bases.

a-Phenyl-β-6-diazo-3-methoxycinnamic acid was obtained in the form of the sulphate from the last-mentioned substance; the sulphate crystallises in yellow prisms which explode at 140—150°. On boiling the aqueous solution of the sulphate and gradually adding sodium carbonate, *2-methoxyphenanthrene-9-carboxylic acid* is obtained; it crystallises in lustrous prisms or needles melting at 228°, and exhibits in solution a blue fluorescence; the ammonium, silver, ferric, cupric, and lead salts are crystalline and sparingly soluble. *2-Methoxyphenanthrene* is prepared from the acid by distilling it under 100 mm. pressure; it crystallises in lustrous leaflets melting at 99°, and, in solution, exhibits a faint blue fluorescence; the *picrate* crystallises in orange needles melting at 124°.

[With AUGUST KLEIN.]—From the sulphonic acids obtained from phenanthrene, two were isolated by fractional crystallisation of the lead salts, which crystallise respectively with 2 and 3 H_2O. From the sulphonic acid, which corresponds with the lead salt, crystallising with $2H_2O$, a *phenanthrol* was prepared by fusion with 50 per cent. potassium hydroxide; it crystallises in lustrous leaflets melting at 168°; its *acetyl* derivative crystallises in needles melting at 141°; its methyl ether is identical with the 2-methoxyphenanthrene just described. The hydroxyl group is therefore in position 2. This phenanthrol is identical with the compound obtained by Werner and Kunz (Abstr., 1901, i, 696) from phenanthrylamine, the constitution of which is therefore confirmed.

2-Methoxyphenanthrene, unlike the 3- and 4-derivatives, yields only a *monobromo*-derivative, which crystallises in needles melting at 176°. On oxidising 2-acetoxyphenanthrene with chromic acid, a *quinone*, $C_{16}H_{10}O_4$, is formed as yellowish-red crystals melting at 222°.

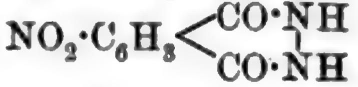
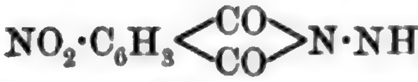
The lead phenanthrenesulphonate crystallising with $3H_2O$ yields 3-phenanthrol (Abstr., 1900, i, 487), which was recognised by preparation of the acetyl derivative and methyl ether (Abstr., 1900, i, 233). The latter gives a *dibromo*-derivative which crystallises in pale red needles melting at 150°. 3-Acetoxyphenanthrene, on oxidation, yields a *quinone*, $C_{16}H_{10}O_4$, which forms yellow leaflets melting at 206°; from the latter, on hydrolysis, is obtained *3-phenanthrolquinone*, $C_{14}H_8O_3$, crystallising in yellowish-red needles which begin to decompose at 315° and finally melt at 330°. The temperatures quoted are corrected. K. J. P. O.

The Mononitrophthalic Acids. By Marston T. Bogert and Leopold Boroschek (*J. Amer. Chem. Soc.*, 1901, **23**, 740—761).—3-Nitrophthalic acid, when heated in a closed tube, melts at 222°, but in an open tube it decomposes at about 207° with formation of the anhydride. The aniline salt (Graebe and Buenzod, Abstr., 1899, i, 762) crystallises in colourless needles and melts at 185—187°. The acid *o-toluidine* salt, $NO_2\cdot C_6H_3(CO_2H)_2,NH_2\cdot C_6H_4Me$, forms slender, white needles, melts at 181°, and at a slightly higher temperature decomposes into water and the *o*-tolil. The *monoethyl* ester,

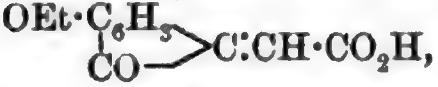
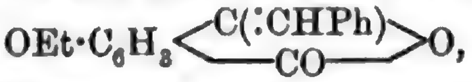
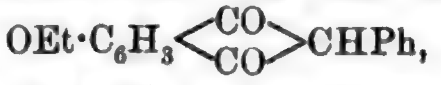
$$NO_2\cdot C_6H_3(CO_2H)\cdot CO_2Et,$$

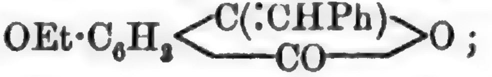
is a white, crystalline substance melting at 157°. The anhydride, obtained by heating the acid at 235—240° for 6—8 hours, crystallises in colourless needles and melts at 163°. The *imide*, prepared by the action of heat on the ammonium hydrogen salt, crystallises in pale yellow, lustrous needles, melts at 215—216°, and furnishes a white, crystalline *potassium* salt. The *amide* melts and decomposes at 200—201° with formation of the imide. 3-*Nitrophthalamic acid*,

$$NO_2\cdot C_6H_3(CO_2H)\cdot CO\cdot NH_2,$$

obtained by heating the imide with baryta water at 80°, melts at 156° with production of the imide. The *ethylimide* crystallises in long, yellow needles and melts at 105°. The anil melts at 137°. The *anilic acid*, $NO_2\cdot C_6H_3(CO_2H)\cdot CO\cdot NHPh$, forms pale yellow needles and melts at 180° with formation of the anil. The o-, m- and p-*nitroanils* melt at 167°, 219°, and 249° and the o-, m- and p-*tolils* at 145°, 129°, and 154° respectively. The *hydrazide*,  $NO_2\cdot C_6H_3\Big<\begin{matrix}CO\cdot NH\\ \vert\\ CO\cdot NH\end{matrix}$ or  $NO_2\cdot C_6H_3\Big<\begin{matrix}CO\\ CO\end{matrix}\Big>N\cdot NH_2$, forms pale yellow, microscopic crystals and melts and decomposes at about 320°. When 3-nitrophthalic anhydride is heated with phosphorus pentachloride, 3-chlorophthalic anhydride is produced, which on boiling with dilute hydrochloric acid yields the corresponding acid melting at 186°. 3-*Chlorophthalimide* crystallises in white needles; when heated in an open tube, it sublimes, but in a closed tube it melts at 118—120°.

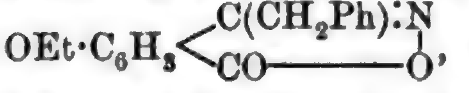
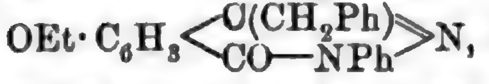
4-Nitrophthalic acid is best prepared by the oxidation of *p*-nitrophthalide with alkaline potassium permanganate. When an alcoholic solution of 4-nitrophthalic anhydride is boiled for 8 hours, an *ethyl* ester, $NO_2\cdot C_6H_3(CO_2H)\cdot CO_2Et$, is produced which melts at 141—150°, and appears to be an isomeride of the ester (m. p. 127—128°) obtained by Miller (Abstr., 1882, 404) by the action of hydrogen chloride on an alcoholic solution of the acid. The *imide* crystallises in pale yellowish-brown flakes, melts at 197°, and yields a *potassium* salt. The *amide* melts at 200° with formation of the imide. The *ethylimide* forms pale yellow scales and melts at 111—112°. The anil melts at 194°. The *anilic acid* forms pale yellow crystals, and melts at 181° with production of the anil. The o-, m- and p-*nitroanils* melt at 233°, 243°, and 251—253°, and the o-, m- and p-*tolils* at 160°, 197°, and 165° respectively. The p-*tolilic acid* crystallises in white needles, and melts at 172° with formation of the *p*-tolil. The *hydrazide* forms small yellow crystals, gives a white sublimate at 270°, darkens at 280°, and remains unmelted at 300°. 4 : 4′-*Azophthalic acid*, obtained by reducing 4-nitrophthalic acid with sodium amalgam, forms a salmon-coloured, crystalline powder, does not melt at 360°, and furnishes a red, crystalline *silver* salt which is insoluble in hot water; if, however, the azophthalic acid is prepared by the oxidation of 5 : 5′-azophthalide with potassium permanganate, it melts and decomposes at 285—300°, and yields a silver salt soluble in hot water. 5 : 5′-*Azophthalide*, obtained by the reduction of *p*-nitrophthalide with sodium amalgam, forms small, red crystals and melts and decomposes at 260—280°. E. G.

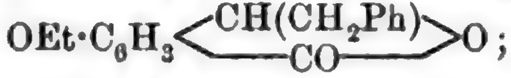
Derivatives of the Two Nitrophthalic Acids. By PAUL ONNERTZ (*Ber.*, 1901, **34**, 3735—3747).—*β-Ethoxyphthalylacetic acid*,  $\begin{matrix}OEt\cdot C_6H_3\\ | \\ CO\end{matrix}{>}C{:}CH\cdot CO_2H$, prepared by heating ethoxyphthalic anhydride with acetic anhydride and sodium acetate, forms small, yellow needles, melts at 246—248° and does not dissolve in water. *Benzylidene-β-ethoxyphthalide*,  $OEt\cdot C_6H_3{<}\begin{matrix}C(:CHPh)\\ CO\end{matrix}{>}O$, prepared from ethoxyphthalic anhydride and phenylacetic acid, forms prismatic crystals and melts at 133—134°. When warmed with potassium hydroxide, it is converted into 4-(or 5-)*ethoxydeoxybenzoin-2-carboxylic acid*, $CO_2H\cdot C_6H_3(OEt)\cdot CO\cdot CH_2Ph$, which crystallises from a large bulk of hot water in minute, white prisms and melts at 95—96°; with alcoholic potassium hydroxide or sodium ethoxide, on the other hand, *6-ethoxy-2-phenyl-1 : 3-diketohydrindene*,  $OEt\cdot C_6H_3{<}\begin{matrix}CO\\ CO\end{matrix}{>}CHPh$, is obtained, which crystallises from boiling alcohol in yellow plates and melts at 172°; with alcoholic ammonia, 4-(or 5-)*ethoxydeoxybenzoin-2-carboxylamide* is formed, which crystallises from aqueous alcohol in well-formed, rhombic prisms, melts at 149—151°, and is converted by acetyl chloride into *benzylidene-β-ethoxyphthalimidine*,



$$OEt\cdot C_6H_3{<}\begin{matrix}C(:CHPh)\\ CO\end{matrix}{>}O\ ;$$

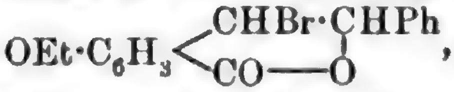
this separates from dilute acetic acid in yellow flakes and melts at 160—162°.

With hydroxylamine, ethoxydeoxybenzoincarboxylic acid gives the *oximino-lactone* of *benzyl*-4-(or 5-)*ethoxyphenylketoxime-2-carboxylic acid*,  $OEt\cdot C_6H_3{<}\begin{matrix}C(CH_2Ph){:}N\\ CO\text{———}O\end{matrix}$, which crystallises from alcohol in long, transparent, prismatic tablets and melts at 112°. With phenylhydrazine, it gives 6-(or 7-)*ethoxy-1-benzyl-3-phenylphthalazone*,  $OEt\cdot C_6H_3{<}\begin{matrix}C(CH_2Ph)\\ CO\text{—}NPh\end{matrix}{>}N$, which crystallises from hot alcohol in pale yellow needles and melts at 126—127°. With sodium amalgam, the first product is *a-hydroxy*-4-(or 5-)*ethoxydibenzyl-2-carboxylic acid*, $OEt\cdot C_6H_3(CO_2H)\cdot CH(OH)\cdot CH_2Ph$, which readily, passes by loss of a molecular proportion of water, into *benzyl-β-ethoxyphthalide*,



$$OEt\cdot C_6H_3{<}\begin{matrix}CH(CH_2Ph)\\ CO\end{matrix}{>}O\ ;$$

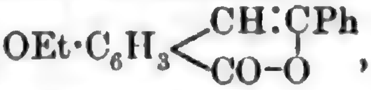
this crystallises from alcohol in microscopic prisms and melts at 87—88°. 4-(or 5-)*Ethoxystilbene-2-carboxylic acid*, $OEt\cdot C_6H_3(CO_2K)\cdot CH{:}CHPh$, isomeric with the preceding compound, is formed when the hydroxy-acid is heated with potassium hydroxide at 213°; it crystallises from alcohol in small needles and melts at 172°. 4- (or 5-)*Ethoxydibenzyl-2-carboxylic acid*, $OEt\cdot C_6H_3(CO_2H)\cdot CH_2\cdot CH_2Ph$, prepared by reducing ethoxystilbenecarboxylic acid with sodium amalgam, separates from alcohol in long, silky needles and melts at 117°. 4-*Bromo*-6-(or 7-) *ethoxy-3-phenyldihydroisocoumarin*,



$OEt\cdot C_6H_3{<}\begin{array}{l}CHBr\cdot CHPh\\ CO—O\end{array}$

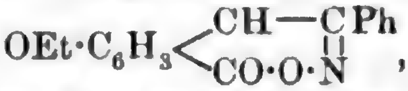
, prepared by the action of bromine on ethoxystilbenecarboxylic acid, crystallises from absolute alcohol in colourless needles and melts at 103°.

6- (or 7-)*Ethoxy-3-phenylisocoumarin*,



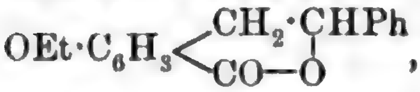
$OEt\cdot C_6H_3{<}\begin{array}{l}CH:CPh\\ CO-O\end{array}$

, prepared by distilling the preceding compound, separates from alcohol in large, flat crystals and melts at 144—145°. 4′- (or 5′-)*Ethoxydeoxybenzoin-2′-carboxylic acid*, $OEt\cdot C_6H_3(CO_2H)\cdot CH_2\cdot COPh$, prepared by the action of potassium hydroxide on the preceding compound, crystallises from dilute alcohol in long, silky needles and melts at 172—173°; with hydroxylamine, it gives the *oximic* acid, $OEt\cdot C_6H_3(CO_2H)\cdot CH_2\cdot CPh:NOH$, which separates from dilute alcohol in small, pale rose-coloured, pointed crystals, and melts and intumesces at 174°; when this is allowed to cool after fusion and crystallised from acetic acid, the *oximinolactone*,



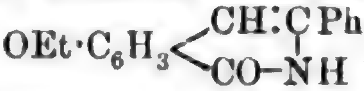
$OEt\cdot C_6H_3{<}\begin{array}{l}CH—CPh\\ CO\cdot O\cdot N\end{array}$

, is obtained in clear, rhombic tablets melting at 164·5—166°. The *phenylhydrazone*, $CO_2H\cdot C_6H_3\cdot CH_2\cdot CPh:N_2HPh$, prepared by the action of phenylhydrazine on the ketonic acid, separates from alcohol in white, felted flakes and melts at 187°. 6-(or 7-)*Ethoxy-3-phenyldihydroisocoumarin*,



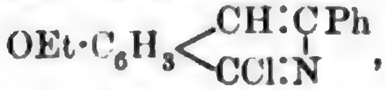
$OEt\cdot C_6H_3{<}\begin{array}{l}CH_2\cdot CHPh\\ CO—O\end{array}$

, prepared by reducing the ketonic acid with sodium amalgam, crystallises from dilute alcohol in microscopic tablets and melts at 83—84°; by heating the crude alkaline solution obtained on reduction, the isomeric β-ethoxystilbenecarboxylic acid is formed, as in the case of the isomeride described above. 6-(or 7-)*Ethoxy-3-phenylisocarbostyril*,



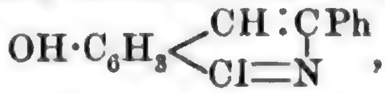
$OEt\cdot C_6H_3{<}\begin{array}{l}CH:CPh\\ CO-NH\end{array}$

, prepared by the action of ammonia on ethoxyphenyl*iso*coumarin, forms minute, pointed crystals and melts at 161°. 1-*Chloro*-6-(or 7-)*ethoxy-3-phenylisoquinoline*,



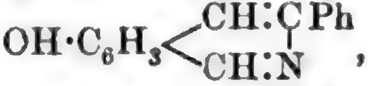
$OEt\cdot C_6H_3{<}\begin{array}{l}CH:CPh\\ CCl:N\end{array}$

, prepared by the action of phosphorus oxychloride on ethoxyphenyl*iso*carbostyril, crystallises from hot alcohol in pointed prisms and melts at 113—114°. 1-*Iodo*-6-(or 7)-*hydroxy-3-phenylisoquinoline*,



$OH\cdot C_6H_3{<}\begin{array}{l}CH:CPh\\ CI=N\end{array}$

, prepared by the action of hydriodic acid and phosphorus on the preceding compound, forms yellowish, pointed crystals and melts at 141—143°; by the further action of hydriodic acid and phosphorus, the *hydriodide* of 6-(or 7-) *hydroxy-3-phenylisoquinoline*,



$OH\cdot C_6H_3{<}\begin{array}{l}CH:CPh\\ CH:N\end{array}$

, is obtained in yellow, microscopic needles which darken at 180°, become deep brown-red at 190°, sinter at 196°, and melt and decompose at 203—204°;

the *base* crystallises from a mixture of alcohol and light petroleum in microscopic, felted prisms, which sinter at 190—191° and melt at 196—197° to a yellowish-brown liquid; the *hydrochloride* forms long, silky prisms; the *platinichloride* separates from alcohol in golden-yellow needles, sinters at 253°, and melts at 267—269°; the *picrate* crystallises in long, yellow needles and melts at 211—212°.

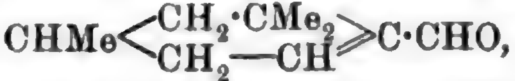
a-Aminophthalic acid, $NH_2 \cdot C_6H_3(CO_2H)_2$, is a yellow, crystalline powder, dissolves readily in acids and alkalis, darkens at 174°, sinters at 179—181°, and melts at 184—186° with liberation of carbon dioxide; the *copper* salt crystallises in small, green, sparingly soluble tablets. *Methyl a-methoxyphthalate*, $OMe \cdot C_6H_3(CO_2Me)_2$, crystallises from hot water in small needles and melts at 71°. T. M. L.

Ethereal Carbonyldiphenylglycinates. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 121198).—*Ethyl carbonyldiphenylglycinate*, $CO(NPh \cdot CH_2 \cdot CO_2Et)_2$, prepared by passing carbonyl chloride through melted ethyl phenylglycinate, is separated from the soluble hydrochloride of the unaltered ester by treatment with water; it melts at 57°. The corresponding *methyl* ester is obtained in a similar manner. These substances are readily converted into indigotin (compare Abstr., 1901, i, 714). G. T. M.

Artemisin. By MARTIN FREUND and LUDWIG MAI (*Ber.*, 1901, **34**, 3717—3719).—As a lactone, artemisin dissolves in dilute aqueous barium hydroxide, and on adding silver nitrate to a solution of the soluble barium salt so formed, the *silver* salt, $C_{15}H_{19}O_5Ag,2H_2O$, is precipitated; the derived *methyl* ester, $C_{16}H_{22}O_5$, crystallises from alcohol and melts and decomposes at 180°. On distilling artemisin with zinc dust, a *dimethylnaphthalene* boiling at 264° is formed, which is not identical with that obtained by Cannizzaro from santonin, as its *picrate* melts at 119°, not at 139°; it is perhaps identical with the β-dimethylnaphthalene of Emmert and Reingruber (b. p. 264°, picrate m. p. 118°, Abstr., 1882, 733). W. A. D.

So-called Basic Bismuth Gallate of the Codex. By PAUL THIBAULT (*J. Pharm. Chim.*, 1901, [vi], **14**, 487—493. Compare Abstr., 1893, i, 643; 1901, ii, 106).—An excess of crystallised gallic acid is added to pure hydrated bismuth oxide (the anhydrous oxide has no action) previously mixed with water, and the mixture is well stirred. The action is complete at the end of 24 hours, and the product, after being washed and dried, is amorphous and opaque, and has the composition $C_7H_7O_7Bi$. If the mixture is left for a fortnight, the bismuth compound appears in the form of small, yellow, micaceous crystals, which have the same composition as the amorphous compound. Sulphuric acid diluted to a fifth dissolves this compound in the cold, but when diluted to a tenth only dissolves it when heated. It dissolves in a solution of potassium hydroxide, and the residue left after evaporation and removal of the excess of potassium hydroxide is of definite composition and corresponds with the formula $K_2BiC_7H_7O_7,2H_2O$. From a consideration of the properties of this potassium salt, the so-called basic bismuth gallate must be regarded, not as a bismuth salt, but as a bismuthigallic acid. The action of sodium hydroxide is similar to that of potassium hydroxide. H. R. LE S.

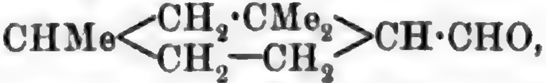
Preparation of Hydrogenised Cyclic Aldehydes. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 121975. Compare Abstr., 1900, i, 691, 692).—*Trimethyltetrahydrobenzaldehyde*,



$$CHMe<\begin{array}{l}CH_2\cdot CMe_2\\ CH_2—CH\end{array}\geqslant C\cdot CHO,$$

produced by oxidising trimethyltetrahydrobenzylaniline with chromic acid mixture in boiling aqueous solution, is a colourless oil volatile in steam and boiling at 90—91° under 18 mm. pressure; it is isomeric with *cyclo*citral; its odour when concentrated resembles that of cedar wood, but when diluted recalls that of violets.

2 : 2 : 4-*Trimethylhexahydrobenzaldehyde*,

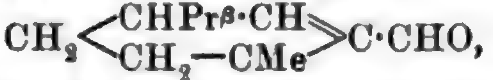


$$CHMe<\begin{array}{l}CH_2\cdot CMe_2\\ CH_2—CH_2\end{array}>CH\cdot CHO,$$

prepared in a similar manner from trimethylhexahydrobenzylaniline, is a colourless, pungent oil.

2-*Methyl*-5-iso*propylhexahydrobenzaldehyde*, derived either from methyl*iso*propylhexahydrobenzylethylamine or methyl*iso*propylhexahydrobenzylaniline, is a colourless, pungent oil, which, when diluted, has the odour of geranium oil.

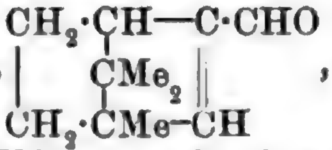
2-*Methyl*-5-iso*propyltetrahydrobenzaldehyde*,



$$CH_2<\begin{array}{l}CHPr^{\beta}\cdot CH\\ CH_2—CMe\end{array}\geqslant C\cdot CHO,$$

obtained from 2-methyl-5-*iso*propyltetrahydrobenzylideneaniline, is a colourless oil boiling at 98° under 15 mm. pressure and has an odour of orange oil.

Camphenaldehyde,



$$\begin{array}{l}CH_2\cdot CH—C\cdot CHO\\ \quad\quad CMe_2 \quad \|\\ CH_2\cdot CMe—CH\end{array}$$

, produced from the corresponding amine, $C_{10}H_{15}\cdot NHPh$, is a colourless pungent oil boiling at 104—105° under 15 mm. pressure. G. T. M.

Acetates derived from the Aromatic Aldehydes. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P. 121788).—Aromatic compounds containing methyl groups are oxidised to aldehydes by chromic acid or its salts in the presence of acetic anhydride, the products being shielded from further oxidation by conversion into the corresponding acetyl esters.

p-*Nitrobenzylidene diacetate*, $NO_2\cdot C_6H_4.CH(OAc)_2$, results from the action of chromic acid on a cold solution of *p* nitrotoluene, sulphuric acid, acetic anhydride, and acetic acid; it crystallises from alcohol in truncated prisms and melts at 125°. The corresponding *diacetate* from *o*-nitrotoluene melts at 87—88°.

The *tetra-acetate*, $C_6H_4[CH(OAc)_2]_2$, derived from iso*phthalaldehyde* and produced by the oxidation of *m*-xylene by the preceding method, separates in needles melting at 101°. The *tetra-acetates* derived from *o*- and *p*-xylene melt respectively at 126—127° and 164—165°. These acetates on hydrolysis yield the corresponding aldehydes. G. T. M.

New Aromatic Aldehyde occurring in Eucalyptus Oils. By HENRY G. SMITH (*J. Roy. Soc. N.S. Wales*, 1900, 286—295).—The crude oil of *Eucalyptus hemiphloia* was distilled; after the constituents boiling below 190° had been removed, the residue, on treatment with sodium hydrogen sulphite, yielded a crystalline mass which, when decomposed with sodium carbonate, furnished an aldehyde. This aldehyde (*aromadendral*), $C_{10}H_{14}O$, boils at 210°, has a yellowish colour, a sp. gr. 0·9477 at 15°/15°, and $[\alpha]_D$ – 49·19; it can also be obtained from the higher boiling fractions of the oils of *E. cneroifolia*, *E. albens*, and *E. Woolsiana*. Its *oxime* forms colourless crystals and melts at 84°. The *phenylhydrazone* melts and decomposes at 105°. The β-naphthacinchonic *acid* melts and decomposes at 247°. When the aldehyde is oxidised with potassium dichromate, crystals of *aromadendric acid*, $C_9H_{13}\cdot CO_2H$, are obtained; it melts at 110°, is soluble in alcohol, ether, or hot water, and furnishes *ammonium*, *silver*, and *copper* salts. If the aldehyde is oxidised with potassium permanganate, eucalyptol is produced, together with an *acid* which is easily soluble in alcohol or ether, melts at 259—260°, and is thereby converted into the anhydride. This *anhydride* melts at 152°, sublimes readily, and is very soluble in alcohol, ether, or boiling water. E. G.

Dialdehydes resulting from Aldehydes and Aromatic Hydroxyaldehydes. I. Action of Benzaldehyde on Vanillin. By M. ROGOFF (*Ber.*, 1901, **34**, 3881—3884).—*Benzylidenedivanillin*, $CHPh[C_6H_2(OMe)(OH)\cdot CHO]_2$, prepared by condensing benzaldehyde with vanillin in presence of zinc chloride, forms white, microscopic needles, melts at 221·5—222·5° (corr.) to a reddish-brown liquid, reduces ammoniacal silver solution in the cold and Fehling's solution on warming, dissolves in sodium hydroxide, ammonia, and sodium carbonate, but not in sodium hydrogen carbonate, and is readily soluble in most organic solvents, but only sparingly so in benzene or ether, and not at all in light petroleum. The *hexa-acetate*, $C_{35}H_{16}O_{14}$, prepared by the action of acetic anhydride and sulphuric acid on the preceding compound, crystallises from 60 per cent. alcohol, melts at 159·5—162·5° (corr.), and is not hydrolysed by heating for 10 minutes with 15 per cent. sodium hydroxide. T. M. L.

[Oxidation of Mesityl Methyl Ketone and ψ-Cumyl Methyl Ketone]. By L. VAN SCHERPENZEEL (*Rec. Trav. Chim.*, 1901, [ii], **20**, 328—330).—In a previous paper (Abstr., 1901, i, 328), the author made no mention of the isolation by Meyer and Molz (Abstr., 1897, i, 474) of mesitylglycollic acid during the oxidation of mesityl methyl ketone.

ψ-Cumyl methyl ketone, which melts at 11° and boils at 245—250°, gives, on oxidation with potassium permanganate at 15°, according to Claus' method (Abstr., 1890, 981), ψ-cumylglyoxylic acid without any ψ-cumylglycollic acid; the acid obtained melted at 61—62° and the melting point could not be raised to 75°, that given by other authors. W. A. D.

Two Stereoisomeric Benzylidenedeoxybenzoins. By HANS STOBBE and KARL NIEDENZU (*Ber.*, 1901, **34**, 3897—3913).—When a mixture of deoxybenzoin and benzaldehyde in mol. proportion is saturated with hydrogen chloride, according to Klages and Knoevenagel's method (Abstr., 1893, i, 350, 353), besides chlorobenzyldeoxybenzoin (which melts at 172—172·5° and not at 182—185°), benzamarone (m. p. 215—216°) and a ketone, *iso*benzylidenedeoxybenzoin (phenyl α-phenylcinnamyl ketone), CHPh:CPh·COPh (m. p. 88—89°), are formed. The latter is stereoisomeric with benzylidenedeoxybenzoin, formed by the action of concentrated alkali hydroxides on the chloro-compound just mentioned (compare Klages and Knoevenagel) and identical with the ketone, β-$C_{21}H_{16}O$, obtained by distilling benzamarone (Klingemann, Abstr., 1893, i, 353); it is formed to the extent of 60—70 per cent. when hydrogen chloride is passed into a mixture of deoxybenzoin (2 mols.) and benzaldehyde (1 mol.) at a temperature of 75—80°, and crystallises in yellow prisms or white needles. It is distinguished from its isomeride by the fact that it dissolves in sulphuric acid with a purple-red colour, which in a few seconds becomes violet, and, later, dark green; addition of water produces an orange-red coloration; benzylidenedeoxybenzoin, on the other hand, dissolves in sulphuric acid with an orange-red coloration which does not change; on addition of water, the solution becomes colourless. After prolonged heating with phenylhydrazine, the *iso*-compound yields the phenylhydrazone of benzylidenedeoxybenzoin (m. p. 163—164°). On oxidation with nitric acid, both substances yield benzoic acid and benzil (or their nitro-derivatives). By heating either of the ketones alone at 160°, or by boiling or by exposing to light a solution of either in benzene in the presence of iodine, a mixture of the two ketones is always obtained, partial transformation of the one into the other having taken place. With bromine, *iso*benzylidenedeoxybenzoin gives the same dibromo-compound (m. p. 134—135°) as does benzylidenedeoxybenzoin. With deoxybenzoin, the normal reacts far more readily than the *iso*-compound to form benzamarone.

On treating the normal ketone in benzene solution with hydrogen chloride, chlorobenzyldeoxybenzoin (m. p. 172°) and the *iso*ketone are formed; similarly, the *iso*ketone yields, but more slowly, the same chloro-compound, together with a certain amount of the normal ketone. The chloro-compound (m. p. 135°) obtained by Klingemann (*loc. cit.*) was not found.

From these facts, the conclusion is drawn that under the action of hydrogen chloride, benzaldehyde and deoxybenzoin first form *iso*benzylidenedeoxybenzoin, which is transformed into the normal ketone; the latter then combines with hydrogen chloride, forming chlorobenzyldeoxybenzoin. K. J. P. O.

Constitution of Piceol. By ERNEST CHARON and DÉMÉTRIUS ZAMANOS (*Compt. rend.*, 1901, **133**, 741—743. Compare Tanret, Abstr., 1894, i, 616).—It is shown that piceol (obtained from a glucoside, picein, occurring in the leaves of *Pinus picea*) is *p*-hydroxyacetophenone. From piceol and synthetical *p*-hydroxyacetophenone, the same oxime, phenylhydrazone, and semicarbazone, were obtained. The *oxime*,

$$OH\cdot C_6H_4\cdot CMe:N\cdot OH,$$

crystallises in colourless needles melting at 143°; the phenylhydrazone melts at 148°; the *semicarbazone* crystallises in colourless needles and melts at 199°.

The authors have prepared *p*-hydroxyacetophenone from anisole; this is first converted into *p*-methoxyacetophenone by the action of acetyl chloride and aluminium chloride, and the methoxy-group in the latter is then converted into hydroxyl by passing hydrogen bromide into hot water containing the *p*-methoxyacetophenone in suspension.

K. J. P. O.

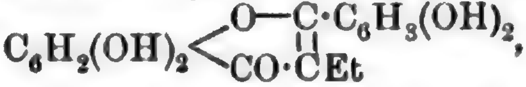
α-Hydroxybenzylideneacetophenone. By F. J. Pond, H. J. York, and B. L. Moore (*J. Amer. Chem. Soc.*, 1901, **23**, 789—796. Compare Abstr., 1900, i, 102).—When bromine is added to an ethereal solution of benzylideneacetophenone, a dibromide separates which melts at 157° (Wislicenus, Abstr., 1900, i, 37); by evaporating the filtrate, a second (or β-) *dibromide* is obtained, which crystallises in small, slender needles and melts at 108—109°. If the α-dibromide (1 mol.) is heated with sodium methoxide (2 mols.), the *methyl ether* of α-hydroxybenzylideneacetophenone is produced as an oil which boils at 206—210° under 12 mm. pressure, and is readily hydrolysed by hydrochloric acid with formation of the α-hydroxy-compound. The *ethyl ether* may be prepared in a similar manner. The α-hydroxybenzylideneacetophenone, obtained as above, is identical with that described by Wislicenus (*loc. cit.*), but the isomeric dibenzoylmethane is not produced under these conditions. The *copper* and *iron* salts are described.

E. G.

α-Ethylluteolin. By Stanislaus von Kostanecki and A. Różycki (*Ber.*, 1901, **34**, 3719—3721. Compare Kostanecki and Lloyd, Abstr., 1901, i, 735).—2 : 4 : 6 : 3′-Tetramethoxy-4′-ethoxybenzoylacetophenone (Diller and Kostanecki, Abstr., 1901, i, 476) interacts with ethyl iodide in boiling alcoholic potassium hydroxide solution to form *3′-methoxy-4′-ethoxybenzoyl-2 : 4 : 6-trimethoxyethylacetophenone*,

$$C_6H_2(OMe)_3\cdot CO\cdot CHEt\cdot CO\cdot C_6H_3(OMe)\cdot OEt;$$

this crystallises from alcohol in white leaflets, melts at 132—133°, and when boiled with concentrated hydriodic acid yields *α-ethylluteolin*,



$$C_6H_2(OH)_2\Big\langle\begin{array}{l}O-C\cdot C_6H_3(OH)_2\\ \qquad\ \|\\ CO\cdot CEt\end{array},$$

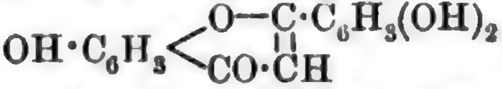
which crystallises from dilute alcohol in pale yellow needles, melts at 286—287°, and yields a *tetra-acetyl* derivative crystallising in white needles and melting at 129—130°.

W. A. D.

3 : 3′ : 4′-Trihydroxyflavone. By Stanislaus von Kostanecki and A. Różycki (*Ber.*, 1901, **34**, 3721—3727).—Previous attempts to prepare this substance have failed (Emilewickz and Kostanecki, Abstr., 1899, i, 368, and Kostanecki and Różycki, *ibid.*, i, 911), but the following method gave the desired result.

3′-Methoxy-4′-ethoxybenzoyl-2 : 4-diethoxyacetophenone,

$$C_6H_3(OEt)_2\cdot CO\cdot CH_2\cdot CO\cdot C_6H_3(OMe)\cdot OEt,$$

which is obtained by heating ethyl ethylvanillate with resacetophenone diethyl ether in presence of sodium, crystallises from alcohol in yellow needles, melts at 134—135°, and with boiling hydriodic acid yields *3 : 3′ : 4′-trihydroxyflavone*,  $OH\cdot C_6H_3\Big\langle\begin{array}{l}O-C\cdot C_6H_3(OH)_2\\ \qquad\ \|\\ CO\cdot CH\end{array}$; the latter crystallises from very dilute alcohol in slightly yellow needles, melts at 326—327°, and yields a *triacetyl* derivative crystallising in white needles and melting at 209—210°.

Benzoyl-2 : 4-*diethoxyacetophenone*, $C_6H_3(OEt)_2\cdot CO\cdot CH_2Bz$, obtained by condensing ethyl benzoate and resacetophenone diethyl ether with sodium, crystallises from alcohol in yellow needles, melts at 120—121°, and is converted by boiling hydriodic acid into 3-ethoxyflavone.

W. A. D.

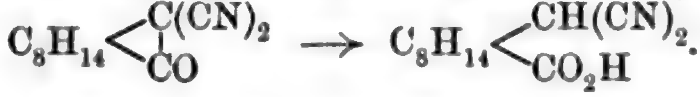
Addition of Alcohols to Quinone. By EMIL KNOEVENAGEL and CARL BÜCKEL (*Ber.*, 1901, **34**, 3993—3998).—When ethyl alcohol is heated with quinone in the presence of zinc chloride, an interaction takes place in which *p*-diethoxyquinone (compare Nietzki and Rechberg, Abstr., 1890, i, 967) and quinol are formed quantitatively. Other primary alcohols (ethyl alcohol, &c.) behave in an analogous manner. In the absence of zinc chloride, no such reaction takes place; other metallic chlorides cannot be substituted for zinc chloride. 2 : 5-*Dibenzoyloxyquinone*, $C_6H_2O_2(OBz)_2$, prepared by heating with benzoyl chloride the *p*-dihydroxyquinone obtained from diethoxyquinone, crystallises in yellow leaflets melting at 174°. 2 : 5-*Dipropyloxyquinone*, $C_6H_2O_2(OPr^a)_2$, crystallises in golden-yellow leaflets melting at 187°. 2 : 5-*Dipropyloxyquinol*, $C_6H_2(OH)_2(OPr^a)_2$, prepared by reducing with stannous chloride the corresponding quinone, crystallises in flattened needles melting at 95°.

K. J. P. O.

Attempted Synthesis of the Camphor Ring as a Contribution to the Tension Theory. By NICOLAI D. ZELINSKY (*Ber.*, 1901, **34**, 3798—3801).—The author has attempted to convert the *cistrans*-form of hexahydroterephthalic acid into a dicyclic ketone, that is, a compound containing the camphor ring. On heating the barium salt of the acid with calcium carbonate, hydrogen is evolved and benzene obtained, together with a small quantity of a substance of a ketonic nature. This substance yielded a *semicarbazone*, $C_8H_{13}ON_3$, which crystallised in white scales melting at 209—210° and is probably the derivative of a dicyclic heptanone.

K. J. P. O.

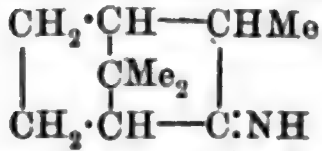
Action of Cyanogen Chloride on Sodium Camphor. By H. DUVAL (*Bull. Soc. Chim.*, 1901, [iii], **25**, 953—955).—By the action of cyanogen chloride on sodium camphor, a *compound*, $C_{12}H_{16}O_2N_2$, was obtained; this crystallises from hot water (which dissolves about 9 grams per litre) in colourless needles, melts at 168°, and has acid properties. It is regarded as a product of hydrolysis of dicyanocamphor,



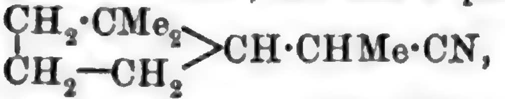
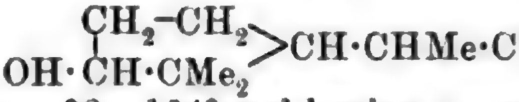
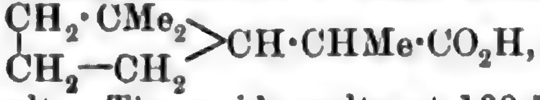
$$C_8H_{14}{<}\begin{matrix}C(CN)_2\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}{<}\begin{matrix}CH(CN)_2\\ CO_2H\end{matrix}.$$

T. M. L.

Transformation and Oxidation of Fenchoneimine by Atmospheric Oxidation. By FRIEDRICH MAHLA (*Ber.*, 1901, **34**, 3777—3785. Compare Abstr., 1897, i, 85).—Fenchoneimine,

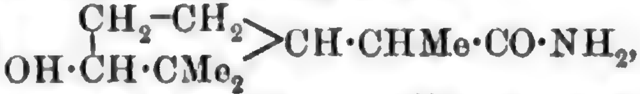


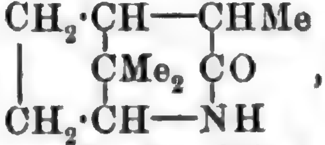
$$\begin{array}{l}CH_2\cdot CH\text{—}CHMe\\ |\quad\;\; CMe_2\;\; |\\ CH_2\cdot CH\text{—}C{:}NH\end{array}$$

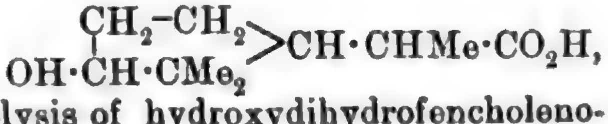
, obtained by treating fenchonenitrimine with 25 per cent. ammonia, boils at 83° under 15 mm. pressure, has $[\alpha]_D$ 76·30° at 19·5°, a sp. gr. 0·9322 at 11·5°, and n_D 1·47809 at 17°; the experimental and calculated values for the molecular refraction are 45·857 and 45·78 respectively. The anhydrous base is stable and remains unchanged even when heated at 200°. The *picrate*, $C_{16}H_{20}O_7N_4$, melts at 202°; *methylfenchoneimine iodide*, $C_{11}H_{20}NI$, is a crystalline product formed from methyl iodide and fenchoneimine dissolved in anhydrous ether. When a stream of dry air is passed through fenchoneimine heated at 105°, the base is partly transformed into *dihydrofenchonitrile*,  $\begin{array}{l}CH_2\cdot CMe_2\\ |\\ CH_2-CH_2\end{array}>CH\cdot CHMe\cdot CN$, and partly oxidised to *hydroxydihydrofenchonitrile*,  $\begin{array}{l}CH_2-CH_2\\ |\\ OH\cdot CH\cdot CMe_2\end{array}>CH\cdot CHMe\cdot CN$; the former compound is an oil boiling at 98—104° and having a pungent odour recalling that of fenchonitrile; it has a_D 25° at 19° in a 100 mm. tube, a sp. gr. 0·8951 at 16·5°, and n_D 1·44743 at 17·5°; the experimental mol. refraction is 45·15°, the calculated value being 45·09. This nitrile, when hydrolysed with boiling 30 per cent. alcoholic potassium hydroxide solution, is only partially decomposed, yielding a mixture of *dihydrofencholeneamide* and *dihydrofencholenic acid*,  $\begin{array}{l}CH_2\cdot CMe_2\\ |\\ CH_2-CH_2\end{array}>CH\cdot CHMe\cdot CO_2H$, the latter in the form of its potassium salt. The amide melts at 130·5° and sublimes slowly at 107°; it is only incompletely hydrolysed by alcoholic potassium hydroxide solution, but when heated at 200° with concentrated hydrochloric acid yields the corresponding carboxy-acid in theoretical quantities. The acid boils at 145—146° under 13 mm. pressure, and has a sp. gr. 0·9816 at 15° and $[a]_D$ 4·3° at 15·5°.

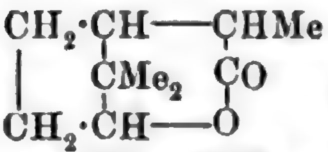
The *silver* salt crystallises from hot water, the ammonium salt is unstable and hygroscopic.

Hydroxydihydrofenchonitrile, which remains in the residue after distilling the oxidation product of fenchimine in a current of steam, is an oil boiling at 153—154° under 23 mm. pressure; it has a sp. gr. 0·9792 at 15°, $[a]_D$ $-8°$ at 18°, n_D 1·46464 at 18°, and mol. refraction 47·11, the calculated value of the last constant being 47·30.

Hydroxydihydrofencholeneamide,  $\begin{array}{l}CH_2-CH_2\\ |\\ OH\cdot CH\cdot CMe_2\end{array}>CH\cdot CHMe\cdot CO\cdot NH_2$, obtained by hydrolysing the preceding nitrile with alcoholic potassium hydroxide solution, crystallises from ethyl acetate and melts at 78°.

Dihydrofencholenic lactam,  $\begin{array}{lll}CH_2\cdot CH & - & CHMe\\ | \quad\; CMe_2 & & CO\\ CH_2\cdot CH & - & NH\end{array}$, is produced together with a non-basic, oily substance by dissolving the preceding amide in warm dilute hydrochloric acid; it separates from aqueous solutions in lustrous, highly refractive crystals and melts at 136—137°. It is identical with Wallach's β-fenchone*iso*oxime obtained from fencholenamide.

4-*Hydroxydihydrofencholenic acid*,  $\begin{array}{l}CH_2-CH_2\\ |\\ OH\cdot CH\cdot CMe_2\end{array}>CH\cdot CHMe\cdot CO_2H$, the ultimate product of the hydrolysis of hydroxydihydrofencholenonitrile, separates from water or ethyl acetate in hard crystals and melts at 113—114°. When heated with water, the acid readily passes



into the *lactone*, ; this substance is volatile in steam and distils alone at 130—150° under 10 mm. pressure, yielding a distillate which solidifies on cooling; it separates from ethyl acetate in well-defined crystals melting at 72°. The lactone is insoluble in sodium carbonate solution, but slowly dissolves in solutions of the alkali hydroxides. G. T. M.

Characterisation and Classification of the Sesquiterpenes. IV.

By Oswald Schreiner and Edward Kremers (*Pharm. Arch.*, 1901, 4, 141—165).—The classification of the terpenes generally is discussed at length.

Oil of ginger was distilled under 30 mm. pressure. The first fraction, boiling below 150°, was redistilled under 32 mm. pressure; the portion collected between 80° and 100° yielded a small quantity of a nitrosite which melts at 105° and is probably not phellandrene nitrite as was supposed by Bertram and Walbaum (Abstr., 1894, i, 201). The second fraction (150—162°) consisted chiefly of zingiberene (Soden and Rojahn, Abstr., 1900, i, 605), which boils at 160—161° under 32 mm. pressure, has a sp. gr. 0·8731 at 20°, n^D 1·49399, and $[a]_D$ $-73·38°$. Its hydrochloride is a white, crystalline substance which melts at 168—169°. The *nitrosite* crystallises in silky needles, melts at 97—98°, and is very unstable. The *nitrosate* is a slightly yellow powder which melts and decomposes at 86—88°. The *nitrosochloride* is a white powder which melts and decomposes at 96—97°.

Caryophyllene hydrochloride (Abstr., 1900, i, 106) is a di-derivative. The sesquiterpene obtained by the action of glacial acetic acid and sodium acetate on it, has a sp. gr. 0·9030 at 20°, n_D 1·49976, and $[a]_D$ $-8·96°$, and is neither regenerated caryophyllene nor clovene.

E. G.

Specific Gravities and Coefficients of Expansion of the Volatile Oils.

By Oswald Schreiner and W. R. Downer (*Pharm. Arch.*, 1901, 4, 165—173).—The sp. gr. of a large number of volatile oils was determined at 15°/15°, 20°/20°, and 25°/25°. The results show that the change in sp. gr. for each degree is comparatively small, and for any one oil is nearly uniform between 15° and 25°, and not very different for different oils. The average change for each degree is 0·00064; this figure applies fairly accurately to all the oils examined with the exception of those of cade and wintergreen. The data obtained have been employed for the calculation of the coefficients of expansion of the oils between 15° and 25°. E. G.

Constituent of Peppermint-like Odour occurring in many Eucalyptus Oils.

By Henry G. Smith (*J. Roy. Soc. N. S. Wales*, 1900, 136—142).—The oil of *Eucalyptus dives*, on fractional distillation, yielded 2 per cent. below 172°, 60 per cent. at 172—200°, 13 per cent. at 200—227°, and 20 per cent. at 227—240°. The last fraction, when treated with sodium hydrogen sulphite, furnished a crystalline compound which, on decomposition with sodium hydroxide, yielded a colourless *oil* of strong peppermint-like taste and odour; this oil is soluble in the usual organic solvents and slightly soluble in water, boils at 224—225°, has a sp. gr. 0·9393 at 17°/15°, $[\alpha]_D$ $-0·35°$ (probably due to the presence of a minute quantity of an aldehyde), and the molecular weight 154. By the action of sodium on an alcoholic solution, a reduction *product* was obtained which crystallises in colourless needles, melts at 155—156°, and is readily soluble in chloroform and slightly so in alcohol, ether, or ethyl acetate.

The fraction of this oil boiling at 227—240° yielded, on hydrolysis, a small quantity of an aromatic alcohol. E. G.

Amyl Eudesmate occurring in Eucalyptus Oils. By HENRY G. SMITH (*J. Roy. Soc. N.S. Wales*, 1900, 72—81).—The oil of *Eucalyptus aggregata* yielded on fractional distillation 26 per cent. boiling at 156—164°, which consisted chiefly of *d*-pinene; 12 per cent. was obtained between 164° and 245°, and 22 per cent. between 245° and 292°; the residue, on cooling, became partly crystalline. Phellandrene and eucalyptol could not be detected. When the oil is hydrolysed with potassium hydroxide, amyl alcohol is produced. If the fraction boiling at 245—292° is shaken with aqueous potassium hydroxide and the alkaline solution acidified with hydrochloric acid, *eudesmic acid*, $C_{13}H_{17}\cdot CO_2H$, separates, which crystallises in rhombic prisms, melts at 160° (uncorr.), is soluble to the extent of 0·0738 per cent. in water at 20°, and readily so in hot water, alcohol, ether, acetone, or chloroform; it sublimes at a high temperature without decomposition. Its *ammonium*, *ferric*, *copper*, and *silver* salts are described. The *bromide*, $C_{14}H_{18}O_2Br_2$, forms colourless crystals and melts at 102—103°. By the action of nitric acid on eudesmic acid, a substance is obtained which crystallises in microscopic needles, melts at 113°, and is probably cumic acid.

The amount of amyl eudesmate present in the oil is 57·7 per cent.

E. G.

Oriental Storax. By ALEXANDER TSCHIRCH and LEOPOLD VAN ITALLIE (*Arch. Pharm.*, 1901, **239**, 506—532).—This is a secretion which forms slowly when incisions are made through the bark of *Liquidambar orientalis* into the wood. It is almost entirely soluble in ether; the residue appears to contain vanillin and also a phlobaphen, since it yields phenol, acetic acid, phloroglucinol and protocatechuic acid when fused with potash. Styrene is present ready formed in the balsam.

From an ethereal solution of the balsam, 0·1 per cent. aqueous sodium carbonate extracts cinnamic acid. Saturated sodium hydrogen sulphite solution then extracts vanillin, which could not be obtained pure, however. Finally, 1 per cent. aqueous sodium hydroxide extracts a resin, at the same time hydrolysing a portion of the latter with formation of a gelatinous mass. In the ethereal solution a mixture of ethyl, phenylpropyl and cinnamyl cinnamates remains.

The resin is hydrolysed by prolonged boiling with aqueous sodium hydroxide to cinnamic acid and a resinol, storesinol; no tannol could be detected. *Storesinol*, $C_{16}H_{26}O_2$, melts at 156—161° when quite pure and dry, otherwise at 93—96°, and is isomeric with benzoresinol (Tschirch and Ludy, Abstr., 1893, i, 480, 666). It is optically active, with $[\alpha]_D$ 13°3′ and 13°32′ in 1 and 2·5 per cent. alcoholic solutions respectively; it gives an absorption band between $\lambda = 0·510$ and $0·540\mu$. It forms a crystalline potassium derivative and also a *methyl ether*, $C_{16}H_{25}O_2Me$, when its concentrated methyl alcoholic solution is boiled for a long time with methyl iodide; it does not form an acetyl or benzoyl derivative, neither will it react with hydroxylamine or phenylhydrazine; it contains no methoxyl or ethoxyl group. When it is mixed with strong sulphuric acid and the mixture diluted with water after a few minutes and heated to boiling, part of the product is insoluble in ether, but soluble in chloroform and is precipitated from the solution in needles by ether. This substance, styrogenin (Mylius, *Pharm. Centralhalle*, 1882, 79), melts above 360° and has the composition $C_{26}H_{40}O_3$. When storesinol is treated with hydrogen bromide in chloroform solution, or heated with 50 per cent. hydrobromic acid in sealed tubes, a *product*, $C_{16}H_{26}O_3$ is obtained, melting at about 280°; the same product is obtained with hydriodic acid, but in no case is the yield good. When storesinol is brominated in acetic acid solution, hydrogen bromide is evolved and an amorphous product is formed containing a varying amount of bromine. Nitric acid of sp. gr. 1·317 oxidises storesinol to picric and oxalic acids and a substance containing nitrogen; chromic acid oxidises it to benzoic acid, dilute aqueous potassium permanganate at 65—70° to phthalic acid and an *acid* which melts at 199°, is insoluble in water, and requires 10·5 c.c. *N*/10 alkali to neutralise 0·357 gram, with phenolphthalein as indicator. Attempts to reduce storesinol with sodium amalgam and with zinc and acetic acid had no result. Fusion with potassium or sodium hydroxide leads to the formation of acetic and salicylic acids. Dry distillation yields phenol and cresol, with benzene, toluene, and probably phenylacetylene. Distillation with zinc dust yields phenol, with benzene and toluene; no naphthalene is formed.

In 100 parts of a sample of the drug, there were contained: Insoluble in ether, 2·4; free cinnamic acid, 23·1; water, 14; aromatic esters, 22·5; styrene and vanillin, 2·0; resin, 36·0. The acid number was 81·0; the saponification number, 179·0; saponification number of the mixture of esters and styrene, 209·0. About half of the combined cinnamic acid was contained in the resin, the rest in the aromatic esters.

C. F. B.

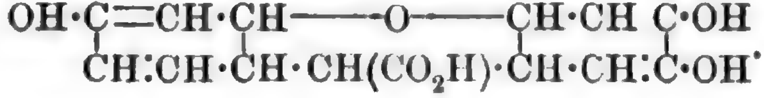
American Storax. By Alexander Tschirch and Leopold van Itallie (*Arch. Pharm.*, 1901, **239**, 532—541).—This substance, also called *sweet gum*, is a secretion which is formed gradually after incisions have been made through the bark of *Liquidambar styraciflua* into the wood. It was examined in the same way as oriental storax (preceding abstract) and found to contain much the same constituents. Of aromatic esters, however, ethyl cinnamate could not be detected with certainty, and the resinol obtained, $C_{16}H_{26}O_2$, has $[\alpha]_D$ 52°, although in all other respects it resembles storesinol; it is therefore regarded provisionally as isomeric with this substance, and is named *styresinol*; it is present both in the free state and as a cinnamate.

In 100 parts of the balsam there are contained : Insoluble in ether, 3·12 ; free cinnamic acid, 23·4 ; aromatic esters, 25 ; styrene and vanillin, 2·0 ; resin, 45·0. The acid number was 89·3 ; saponification number, 192·7 ; the saponification number of the mixture of aromatic esters and styrene, 205·1. Rather more than half of the combined cinnamic acid was contained in the aromatic esters, the rest in the resin. C. F. B.

Rassamala Resin. By ALEXANDER TSCHIRCH and LEOPOLD VAN ITALLIE (*Arch. Pharm*, 1901, **239**, 541—547).—This substance, the product of *Altingia excelsa* (Java), has been subjected to a preliminary examination. It contains benzaldehyde, cinnamic acid and cinnamaldehyde, also a resin and a pentosan ; esters are not present. The balsam is undoubtedly different from either oriental or American storax, with which it has often been confused. C. F. B.

Phoenicein, the Dye from Purple Wood. By ESTELLA KLEEREKOPER (*Chem. Centr.*, 1901, ii, 1085—1086 ; from *Ned. Tijd. Pharm.*, 1901, **13**, 284—288, 303—314. Compare this vol., i, 48).—Further examination has shown that phoenin is not a glucoside. By heating for a long time at 100°, or for an hour at 150—160°, or by the action of dilute acids, it is converted quantitatively into phoenicein with elimination of $1H_2O$. With alkalis, phoenicein, $C_{14}H_{14}O_6$, gives a blue coloration, which becomes violet and finally brown, the alkali salt first formed being reconverted into phoenin and then undergoing further decomposition.

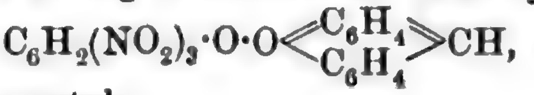
Phoenicein crystallises in minute rods, begins to darken at about 190°, and is easily soluble in methyl or ethyl alcohol and slightly so in water containing mineral acids. With alkalis and ammonia, it forms unstable blue salts. The red colour of the product obtained by boiling phoenin with hydrochloric acid is due to the presence of an unstable compound of phoenicein with the acid ; this compound is decomposed by water, being reconverted into phoenicein. This property of combining with both acids and alkalis is shared by other dyes of the flavone and quercetin groups (compare Perkin, Trans., 1899, **75**, 433), and, like these, phoenicein also gives a blue precipitate with sodium acetate in alcoholic solution. When reduced by zinc dust and glacial acetic acid, it forms a leuco-compound, which is very readily oxidised by exposure to the air, and with aluminium hydroxide and ferric hydroxide it forms blue and brown lakes respectively. By the action of acetic anhydride, an acetyl compound, which apparently contains three acetyl groups, is obtained as a yellowish-white powder, and with nitric acid, phoenicein gives trinitroresorcinol and carbon dioxide. Carbon dioxide is also eliminated by dry distillation or by the action of an alkali, a phenol being probably formed in the latter case. When treated with bromine, phoenicein yields substitution derivatives ; with sulphuric acid, it gives a sulpho-derivative, and with benzoyl chloride, an amorphous benzoyl derivative. The constitution of phoenicein may possibly be :



$$\begin{array}{l} \mathrm{OH{\cdot}C{=}CH{\cdot}CH{-\!-\!-}O{-\!-\!-}CH{\cdot}CH\ C{\cdot}OH} \\ \mathrm{\ \ \ \ \ \ \ CH{:}CH{\cdot}CH{\cdot}CH(CO_2H){\cdot}CH{\cdot}CH{:}C{\cdot}OH} \end{array}$$

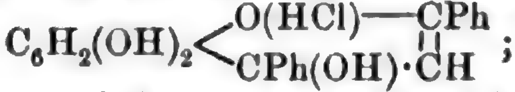
E. W. W.

Basic Properties of Oxygen. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1901, **34**, 3612—3618. Compare Abstr., 1901, i, 658).—Unsaturated hydrocarbons of the ethylene type do not combine with acids. Ferricyanic acid is a strong oxidising agent, and most of the oxonium salts previously described contain small amounts of ferrocyanides. Dimethylpyrone hydrochloride is readily formed when a solution of the base and acid in mol. quantities is evaporated. In concentrated solution, it appears to exist as the salt, but in dilute solution is completely dissociated. As regards basic properties, dimethylpyrone closely resembles carbamide; other oxygen compounds, for example, alcohols and the higher ethers, have basic characteristics analogous to those of nitriles. The latter dissolve in concentrated hydrochloric acid and are thrown down unaltered on dilution. With ferrocyanic, ferricyanic, and cobalticyanic acids, they form crystalline salts. Salts of the following nitriles have been obtained: propionitrile, *n*-butyronitrile, valeronitrile, hexonitrile, and benzonitrile, and benzyl cyanide. J. J. S.

Oxonium Salts. By JOHN THEODORE HEWITT (*Ber.*, 1901, **34**, 3819—3822. Compare *Zeit. physikal. Chem.*, 1901, **34**, 1).—As the result of Werner's publication (this vol., i, 50), attention is drawn to the fact that the author had previously (*loc. cit.*) noted attention to the possibility of the existence of quadrivalent oxygen in xanthydrol salts. These salts, and also those of phenyl-β-dinaphthoxanthydrol in dilute solution exhibit strong fluorescence. Xanthydrol and picric acid yield a *compound*,  $C_6H_2(NO_2)_3\cdot O\cdot O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH$, in the form of dark green, glistening crystals. J. J. S.

Dihydroxy-derivatives of 2 : 4-Diphenyl-1 : 4-benzopyranol. By CARL BÜLOW and WALTHER VON SICHERER (*Ber.*, 1901, **34**, 3916—3929).—Pyrogallol, phloroglucinol, and hydroxyquinol all condense with dibenzoylmethane, yielding various dihydroxy-2 : 4-diphenyl-1 : 4-benzopyranols. These are of a strongly basic nature and the formation of their stable hydrochlorides, sulphates, &c., can only be readily explained by the assumption that the ring oxygen atom is quadrivalent (see also Abstr., 1901, *i*, 400, 599, and 603).

When a stream of dry hydrogen chloride is passed for eight hours into a solution in glacial acetic acid of pyrogallol and dibenzoylmethane, a mass of violet-brown crystals is obtained consisting of the *hydrochloride* of 7 : 8-dihydroxy-2 : 4-diphenyl-1 : 4-benzopyranol,

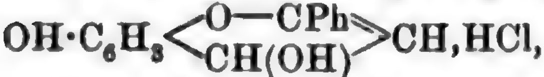


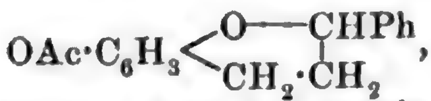
$$C_6H_2(OH)_2<\begin{matrix}O(HCl)—CPh\\ \|\\ CPh(OH)\cdot CH\end{matrix};$$

this crystallises from alcohol containing a little free hydrogen chloride in claret-coloured, felted needles with a coppery lustre, and loses hydrogen chloride when placed in a vacuum or when treated with sodium acetate, yielding the *base* which crystallises in microscopic, violet needles and dissolves in most solvents except water and light petroleum. The constitution of the base is proved by (*a*) the formation of a *triacetyl* derivative, which crystallises from pyridine in short, dark brown prisms and decomposes at (about) 230°, and (*b*) by its hydrolysis to acetophenone, 1 : 2 : 3-trihydroxybenzophenone, pyrogallol, and benzoic acid. The *picrate* crystallises in small, lustrous, brownish-violet needles, which begin to soften at 200° and to melt and decompose at 242°. The *platinichloride* crystallises in lustrous, copper-coloured, felted needles, which begin to soften at 150° and melt at 178°.

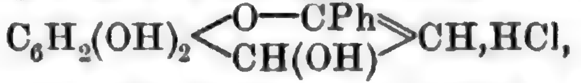
5 : 7-*Dihydroxy*-1 : 4-*benzopyranol*, prepared by condensing phloroglucinol with dibenzoylmethane, is obtained as small, pinkish, cubical crystals; the *hydrochloride* forms lustrous, red, prismatic crystals, is very slightly soluble in water, alcohol, or acetic acid, and decomposes above 260°; the *triacetyl* derivative crystallises from nitrobenzene in dark brown prisms, which gradually decompose above 200°; the 8-*nitroso*-derivative, obtained when the hydrochloride dissolved in acetic acid is treated with nitrous acid, crystallises in slender, reddish-brown needles and decomposes above 230°.

6 : 7-*Dihydroxy*-2 : 4-*diphenyl*-1 : 4-*benzopyranol*, obtained from hydroxyquinol by analogous methods, crystallises from alcohol in ruby-red prisms; the *hydrochloride* crystallises in lustrous, ochre-yellow plates, which, when heated, begin to decompose at 250° and melt and evolve gas at 272°; the *picrate* crystallises in small, red needles, which soften at 220° and melt and decompose at 236°. R. H. P.

New Benzopyranol Derivatives from Benzoylacetaldehyde and Polyhydric Phenols. By CARL BÜLOW and WALTHER VON SICHERER (*Ber.*, 1901, **34**, 3889—3897. Compare Abstr., 1901, i, 400, 559, 603).—7-*Hydroxy*-2-*phenyl*-1 : 4-*benzopyranol hydrochloride*,  $OH\cdot C_6H_3\Big<\begin{matrix}O-CPh\\CH(OH)\end{matrix}\Big>CH,HCl$, is formed when a solution in acetic acid of benzoylacetaldehyde and resorcinol in mol. proportion is saturated with dry hydrogen chloride; it forms brownish-orange crystals melting at 152—153°, dissolves in alkalis with a brownish-red colour, and in solution in concentrated sulphuric acid gives an intense green fluorescence. 7-*Hydroxy*-2-*phenyl*-1 : 4-*benzopyranol*, $C_{15}H_{12}O_3$, prepared by treating an aqueous solution of the hydrochloride with sodium acetate, forms reddish-brown, amorphous flakes; when boiled with aqueous potassium hydroxide it is decomposed into acetophenone, resorcinol, and benzoic acid. The *picrate*, $C_{15}H_{12}O_3,C_6H_3O_7N_3$, crystallises in dark yellow needles melting and decomposing at 232—234°; the *platinichloride* forms small, orange-yellow scales, which darken at 240° and melt and decompose at 244°; the *aurichloride* crystallises in brownish-yellow needles melting and decomposing at 178°. 7-*Acetoxy*-2-*phenyl*-1 : 4-*benzopyranol acetate*, $C_{15}H_{10}O_3Ac_2$, prepared by boiling the hydrochloride with acetic acid and acetic anhydride, forms a violet-grey amorphous powder which begins to melt at 160°. 7-*Methoxy*-2-*phenyl*-1 : 4-*benzopyranol*, $C_{15}H_{11}O_3Me$, prepared by treating the hydrochloride with methyl iodide and sodium methoxide, is a brownish-violet, amorphous powder and does not exhibit fluorescence when dissolved in sulphuric acid.

7-*Acetoxy*-2-*phenyl*-1 : 4-*dihydrobenzopyran*,  $OAc\cdot C_6H_3\Big<\begin{matrix}O-CHPh\\CH_2\cdot CH_2\end{matrix}$, is obtained by reducing the hydrochloride with zinc dust and acetic acid in presence of acetic anhydride, and is an amorphous powder melting, but not sharply, at 112—114°.

5 : 7-*Dihydroxy-2-phenyl*-1 : 4-*benzopyranol hydrochloride*,



$$C_6H_2(OH)_2<\begin{matrix}O-CPh\\CH(OH)\end{matrix}>CH,HCl,$$

prepared by saturating with hydrogen chloride a solution of phloroglucinol and benzoylacetaldehyde, is a brick-red, crystalline powder; the *base* is a brownish-red, amorphous powder.

7 : 8-*Dihydroxy-2-phenyl*-1 : 4-*benzopyranol hydrochloride*, prepared from pyrogallol and benzoylacetaldehyde, was obtained only in an amorphous form, and was converted into the *base* by means of sodium acetate; the latter is a dark brown, amorphous powder. K. J. P. O.

Physiological Properties and Composition of Iboga. Presence of a New Alkaloid, Ibogaine. By J. Dybowski and Edouard Landrin (*Compt. rend.*, 1901, **133**, 748—750).—Iboga is a plant which grows in French Congo. The woody portions are stated by natives to have an effect when consumed similar to that of alcohol. The active principle, *ibogaine*, $C_{52}H_{66}O_2N_6$, is present in the bark and wood and particularly in the roots of the plant, which yielded 0·6 to 1 per cent. of the alkaloid.

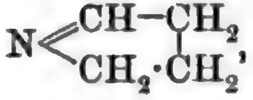
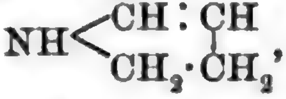
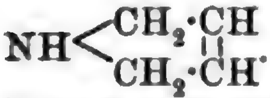
Ibogaine forms long, slightly amber-coloured prisms which melt at 152° and dissolve very readily in alcohol, ether, chloroform, light petroleum, and most other solvents. It is lævorotatory, $[\alpha]_D$ −48°32′ at 15°. The deviation is 1°56′ for 1 gram dissolved in 50 c.c. of alcohol. When exposed to air, ibogaine becomes yellowish-brown and seems to be converted into a non-crystalline substance. Saline solutions are precipitated by Mayer's reagent, by tannin, and by phosphoantimonic acid. Bismuth potassium iodide produces a gold-coloured precipitate. The *sulphate*, *nitrate*, *acetate*, and *benzoate* are neutral, but not crystalline; the *hydrochloride* is crystalline.

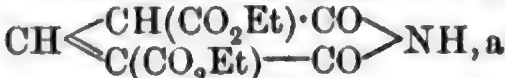
As regards the physiological effect of ibogaine, it was found that large doses produce analogous effects to those resulting from excessive consumption of alcohol. N. H. J. M.

Ipoh Arrow Poisons and some Plants that are used to prepare them. By C. Hartwich and P. Geiger (*Arch. Pharm.*, 1901, **239**, 491—506).—A list is given of plants which are used to prepare poisons with which the heads of arrows are smeared; it is noteworthy that such arrows are almost invariably projected from a blowpipe. The chief of these plants are *Antiaris toxicaria*, which contains antiarin; species of *Strychnos*, containing strychnine and brucine; and *Derris elliptica*, which contains derride.

Samples of poison were examined for these substances: antiarin was detected by the golden-yellow coloration, with subsequent fluorescence, which it gives with sulphuric acid, and by the brown coloration with hot aqueous sodium picrate; derride by the blood-red coloration which it gives with sulphuric acid containing a trace of ferric chloride; strychnine by its reaction with vanadosulphuric acid; brucine by its reaction with nitric acid. Of 25 samples, 2 contained derride, 5 brucine, 11 strychnine, and 21 antiarin. With antiarin there is commonly associated a *substance* closely resembling the fluavil of guttapercha, and also a new alkaloid, *ipohine*, which was found in 12 out of 19 specimens examined. This alkaloid is a virulent poison, causing cessation of the heart's action, much as digitoxin does but a great deal more quickly. Antiarin has a comparatively feeble action.

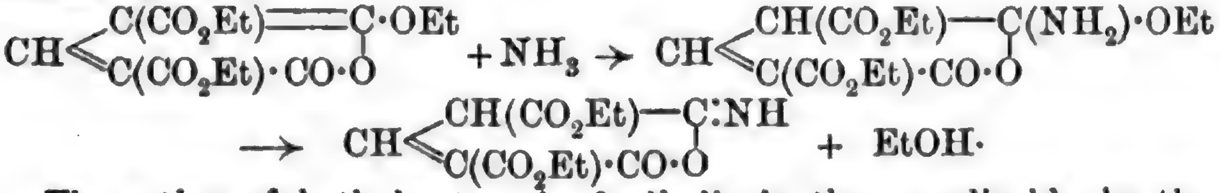
A morphological description of *Antiaris toxicaria* and *Derris elliptica* is given; also the results of the examination of various Indian species of *Strychnos* for strychnine, brucine, and strychnochromin. The last is detected by the green coloration which it gives with concentrated sulphuric acid and with nitric acid; in its occurrence it seems to bear no relation to strychnine or other alkaloids generally. C. F. B.

Conversion of Pyrrole into Pyrroline. By GIACOMO L. CIAMICIAN (*Ber.*, 1901, **34**, 3952—3955. Compare Knorr and Rabe, this vol., i, 54).—The names Δ^1-, Δ^2- and Δ^3-pyrroline are suggested for the three isomeric compounds,  $\mathrm{N}{<}\begin{array}{l}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}$,  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CH{:}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{array}$, and  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CH_2{\cdot}CH}\\ \mathrm{CH_2{\cdot}CH}\end{array}$. The compound obtained by the reduction of pyrrole is most probably Δ^3-pyrroline, as such a constitution harmonises best with Thiele's theory. The reduction is most economically brought about by the aid of zinc dust and acetic acid, since all unaltered pyrrole can be recovered. When hydrochloric acid is employed, all unreduced pyrrole is resinified. Hielscher's base (Abstr., 1898, i, 338) is 1-methyl-Δ^2-pyrroline and differs altogether in properties from Δ^3-pyrroline. J. J. S.

Desmotropism in the Pyridine Series. By GIORGIO ERRERA (*Ber.*, 1901, **34**, 3700—3704).—The three modifications of the imide of ethyl dicarboxyglutaconate,  $\mathrm{CH}{\lessdot}\begin{array}{l}\mathrm{CH(CO_2Et){\cdot}CO}\\ \mathrm{C(CO_2Et){-}CO}\end{array}{>}\mathrm{NH}$, are probably not desmotropic as considered by Guthzeit (Abstr., 1894, i, 71, and 1895, i, 557), for the change of form is not reversible, and the action of dilute alkalis on the imide yields a nitrile,

$$\mathrm{CO_2Et{\cdot}CH(CN){\cdot}CH{:}CH{\cdot}CO_2Et}.$$

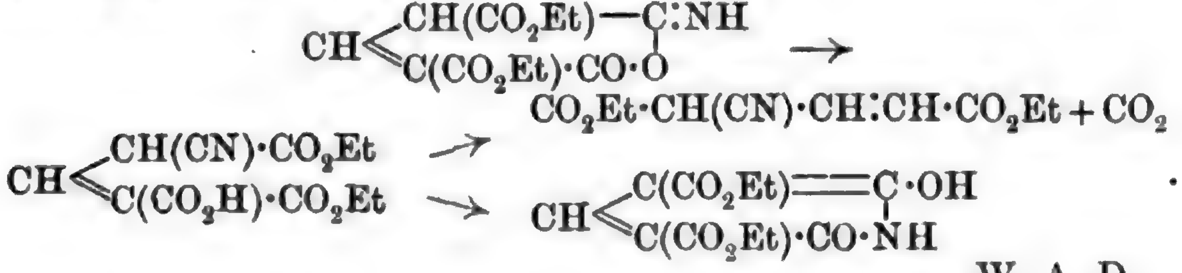
In the light of analogous facts (following abstract) the author considers that the action of ammonia on Guthzeit's coumalin derivative gives an *iso*imide, thus:



$$\mathrm{CH}{\lessdot}\begin{array}{l}\mathrm{C(CO_2Et){=}C{\cdot}OEt}\\ \mathrm{C(CO_2Et){\cdot}CO{\cdot}O}\end{array} + \mathrm{NH_3} \rightarrow \mathrm{CH}{\lessdot}\begin{array}{l}\mathrm{CH(CO_2Et){-}C(NH_2){\cdot}OEt}\\ \mathrm{C(CO_2Et){\cdot}CO{\cdot}O}\end{array}$$

$$\rightarrow \mathrm{CH}{\lessdot}\begin{array}{l}\mathrm{CH(CO_2Et){-}C{:}NH}\\ \mathrm{C(CO_2Et){\cdot}CO{\cdot}O}\end{array} + \mathrm{EtOH}{\cdot}$$

The action of both heat and of alkalis is then explicable by the following scheme:



$$\mathrm{CH}{\lessdot}\begin{array}{l}\mathrm{CH(CO_2Et){-}C{:}NH}\\ \mathrm{C(CO_2Et){\cdot}CO{\cdot}O}\end{array} \rightarrow \mathrm{CO_2Et{\cdot}CH(CN){\cdot}CH{:}CH{\cdot}CO_2Et + CO_2}$$

$$\mathrm{CH}{\lessdot}\begin{array}{l}\mathrm{CH(CN){\cdot}CO_2Et}\\ \mathrm{C(CO_2H){\cdot}CO_2Et}\end{array} \nearrow \quad \rightarrow \mathrm{CH}{\lessdot}\begin{array}{l}\mathrm{C(CO_2Et){=}C{\cdot}OH}\\ \mathrm{C(CO_2Et){\cdot}CO{\cdot}NH}\end{array}$$

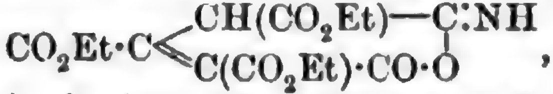
W. A. D.

Action of Halogens and of Ethyl Bromocyanoacetate on Ethyl Sodiocyanoacetate. By GIORGIO ERRERA and F. PERCIABOSCO (*Ber.*, 1901, **34**, 3704—3717. Compare Abstr., 1901, i, 18, and Thorpe and Young, Trans., 1900, **77**, 936).—The action of halogens (iodine in ethereal solution or bromine) on ethyl sodium cyanoacetate gives the same products as the action of ethyl bromocyanoacetate (*loc. cit.*), but the yield is smaller; in addition to ethyl tricyanotrimethylenetricarboxylate (m. p. 119·5°), considerable quantities of *ethyl sodiodicyanoaconitate*, $CO_2Et\cdot CNa(CN)\cdot C(CO_2Et){:}C(CN)\cdot CO_2Et$, are formed; this separates from alcohol in large, yellow, monoclinic crystals, with $\frac{1}{2}H_2O$, melts and decomposes at about 245°, and is hydrolysed by boiling water with loss of $1CO_2$, yielding *ethyl sodiodicyanoglutaconate*, $CO_2Et\cdot CNa(CN)\cdot CH{:}C(CN)\cdot CO_2Et$, which crystallises in needles with $2H_2O$. *Ethyl dicyanoaconitate*,

$$CO_2Et\cdot CH(CN)\cdot C(CO_2Et){:}C(CN)\cdot CO_2Et,$$

obtained by acidifying an aqueous solution of its sodium derivative, crystallises in leaflets, with $\frac{1}{2}H_2O$, melts and decomposes when rapidly heated at 145—146°, and cannot be recrystallised.

If, in the preceding decomposition by acid, the solution of the sodium derivative be very dilute, further hydrolysis occurs, and *ethyl isoiminodicarboxyaconitate*,



$$CO_2Et\cdot C\begin{cases}CH(CO_2Et)—C{:}NH\\ C(CO_2Et)\cdot CO\cdot O\end{cases}$$

, is formed (compare preceding abstract); it does not contain a carboxyl group since it is not acid in character, and crystallises from dilute alcohol in needles, with $1H_2O$, which melt at 70°. By warm dilute alkalis, it is dissolved, and, on acidifying, *ethyl cyanoaconitate*,

$$CO_2Et\cdot CH(CN)\cdot C(CO_2Et){:}CH\cdot CO_2Et,$$

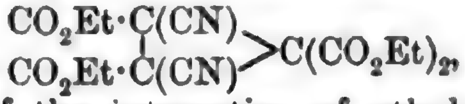
is precipitated as a heavy, yellowish oil with acid properties.

On boiling the *iso*imide with absolute alcohol, it undergoes isomeric change into *ethyl* 5-*carboxy*-2 : 6-*dihydroxycinchomeronate* (*ethyl* 2 : 6-*dihydroxypyridine*-3 : 4 : 5-*tricarboxylate*) or its *iso*dynamic form, *ethyl* 6-*hydroxy*-2-*keto*-$\Delta^{3,5}$-*dihydropyridinetricarboxylate*; the product crystallises from benzene on adding light petroleum in soft, white needles, melts at 137° and is converted by boiling hydrochloric acid of sp. gr. 1·06 into *ethyl* 2 : 6-*dihydroxy*-3 : 4-*cinchomeronate* (*ethyl* 2 : 6-*dihydroxy*-3 : 4-*pyridinedicarboxylate*), which crystallises from benzene or methyl alcohol in white leaflets and melts at 157°; citrazinic acid is also formed.

Monoethyl 2 : 6-*dihydroxycinchomeronate* (*ethyl* 3-*carboxy*-2 : 6-*dihydroxypyridine*-4-*carboxylate* or *ethyl* 4-*carboxy*-2 : 6-*dihydroxypyridine*-3-*carboxylate*), obtained by boiling ethyl 5-carboxydihydroxycinchomeronate with aqueous sodium hydroxide (2 mols.), crystallises from dilute alcohol in small needles and decomposes at 215°.

Ethyl tricyanotrimethylenetricarboxylate (*loc. cit.*) melts when pure at 119·5°; tricyanotrimethylene crystallises from alcohol in white leaflets and melts at 188—189°.

Ethyl dicyanotrimethylenetetracarboxylate,

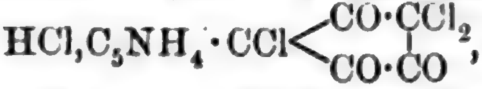


$$\left.\begin{matrix}CO_2Et\cdot C(CN)\\ |\\ CO_2Et\cdot C(CN)\end{matrix}\right>C(CO_2Et)_2,$$

is always formed as one of the products of the interaction of ethyl bromocyanoacetate and sodiocyanoacetate; it crystallises best from alcohol in large, transparent, triclinic crystals and is easily hydrolysed by barium hydroxide to trimethylenetetracarboxylic acid (Schacherl, Abstr., 1885, 1125). W. A. D.

Mixed Methenyl Compounds. IV. Synthesis of 2 : 5-Lutidine [2 : 5-Dimethylpyridine]. By Giorgio Errera (*Ber.*, 1901, **34**, 3691—3700).—*Ethyl ε-cyano-δ-ethoxy-β-hexanone-ε-carboxylamide-γ-carboxylate*, $CH_3\cdot CO\cdot CH(CO_2Et)\cdot CH(OEt)\cdot CMe(CN)\cdot CO\cdot NH_2$, obtained by the interaction of ethyl α-ethoxymethyleneacetoacetate and methylcyanoacetamide (in the form of cyanoacetamide, methyl iodide, and sodium ethoxide in alcoholic solution), crystallises from water in flat, lustrous needles, and melts at 202—203°; it is accompanied by considerable quantities of ethyl 5-cyano-6-hydroxy-2-methylpyridine-3-carboxylate, formed from unchanged cyanoacetamide (Abstr., 1900, i, 43), and of ethyl 6-hydroxy-2 : 5-dimethylpyridine-3-carboxylate (*infra*). *ε-Cyano-δ-ethoxy-β-hexanone-ε-carboxylamide-γ-carboxylic acid* obtained by hydrolysing the ethyl ester, separates from water in hard, opaque, white crystals, and melts and decomposes at 256°; if the hydrolysis is effected by boiling hydrochloric acid, alcohol, ammonia, and carbon dioxide are eliminated and ring formation occurs with the production of *ethyl 6-hydroxy-2 : 5-dimethylpyridine-3-carboxylate*; this crystallises from alcohol in soft, colourless needles, melts at 216—217°, and is easily hydrolysed by boiling dilute alkalis into the corresponding *acid*, which crystallises from glacial acetic acid in slender needles and when rapidly heated melts and decomposes at 300—305°. 6-*Hydroxy*-2 : 5-*dimethylpyridine*, obtained by heating the acid with hydrochloric acid of sp. gr. 1·1 for several hours at 150°, forms monoclinic crystals [$a : b : c = 1{\cdot}54256 : 1 : 1{\cdot}43626$; $\beta = 46°52'57''$], with $\frac{1}{2}H_2O$, and melts at 138—139°; the *potassium* salt, $C_7H_8ONK,5\frac{1}{2}H_2O$, crystallises in lustrous leaflets. 3-*Bromo*-6-*hydroxy*-2 : 5-*dimethylpyridine*, formed by the action of bromine in glacial acetic acid solution, crystallises from alcohol in long, lustrous needles and melts at 218—219°. 2 : 5-*Dimethylpyridine*, formed on distilling its hydroxy-derivative with zinc dust, boils at 159—160°, and yields a crystalline hydrochloride and two *mercurichlorides*, $C_7H_{10}NCl,6HgCl_2$ (small, hard prisms) and $2C_7H_{10}NCl,5HgCl_2$ (long, lustrous needles); the *picrate* melts at 165·5°. W. A. D.

Action of Pyridine Bases on Tetrahalogen Derivatives of Quinones. By Henri Imbert (*Compt. rend.*, 1901, **133**, 937—938).—The compound obtained by the action of pyridine on tetrachloroquinone (this vol., ii, 55), when treated with hydrochloric acid and potassium chlorate, yields a *pyridyltrichlorotriketopentamethylene hydrochloride*,



$$HCl,C_5NH_4\cdot CCl<\begin{matrix}CO\cdot CCl_2\\ |\\ CO\cdot CO\end{matrix}$$

, forming white crystals somewhat soluble in cold water. With phenylhydrazine, it yields a trihydrazone, and with *o*-tolylenediamine it yields an azine. It follows that this oxidation product contains three ketonic groups, two of which are adjacent, and consequently the only admissible formula for the original product (*loc. cit.*) is $C_5NH_4\cdot C_6Cl_2O_2\cdot OH$. C. H. B.

Tertiary and Quaternary Tetrahydro*iso*quinoline Bases; a Contribution to the Stereochemistry of Nitrogen. By EDGAR WEDEKIND and E. OECHSLEN (*Ber.*, 1901, **34**, 3986—3993. Compare Abstr., 1900, i, 155).—2-Methyltetrahydro*iso*quinoline can be readily prepared by reduction of *iso*quinoline methiodide by tin and hydrochloric acid (compare Ferratini, Abstr., 1893, i, 227). It is a colourless oil, distils at 212°, and has strongly basic properties. With ethyl iodoacetate, it forms an *additive* product, $C_{14}H_{20}O_2NI$, which forms yellow crystals melting at 156—157°. 2-*Ethyltetrahydro*iso*quinoline*, C_9NH_9Et, obtained from *iso*quinoline ethiodide, is a pale yellow oil boiling at 225—227°; the *platinichloride* crystallises in reddish-yellow leaflets melting at 169°; the *picrate* in yellow needles melting at 121°; the normal *oxalate* in colourless needles melting at 110°; the *hydriodide* in pale yellow needles melting at 170°; the *additive* compound with ethyl iodoacetate forms small crystals decomposing at 109—110°.

iso*Quinoline benzyliodide* crystallises in large, monoclinic plates [$a:b:c=0{\cdot}5842:1:1{\cdot}3498$; $\beta=82°16{\cdot}5'$], and melts at 175—176°. On reduction, 2-*benzyltetrahydro*iso*quinoline*, $C_{16}H_{17}N$, is obtained as a pale yellow, viscous oil boiling at 194—197° under 18 mm. pressure; the *platinichloride* crystallises in brown pyramids decomposing at 219°; with ethyl iodoacetate, an *additive* compound is obtained as crystals decomposing at 148—149°. *Benzylethyltetrahydro*iso*quinolinium iodide* is formed very readily from 2-ethyltetrahydro*iso*quinoline and benzyl iodide, far more slowly from 2-benzyltetrahydro*iso*quinoline and ethyl iodide; by both methods of preparation a salt is obtained crystallising in large plates which decompose at 133°. The crystals of both specimens are monoclinic, have $\beta=63°40'$, and are in all respects identical. K. J. P. O.

Condensation Products from Aromatic Nitroso-compounds and Methylene Derivatives. By FRANZ SACHS (D.R.-P. 121974).—The *compound* produced by condensing benzyl cyanide and *p*-nitrosophenol in alcoholic sodium hydroxide solution, crystallises in brown needles, melts at 155°, and is converted by dilute mineral acids into the original cyanide and *p*-aminophenol. Corresponding condensation products are obtained from *p*-nitrosophenol and phenylmethylpyrazolone, ethyl acetoacetate, and cyanoacetamide. G. T. M.

Nitroso-*m*-phenylenediamine and Nitroso-2 : 4-tolylenediamine. ERNST TÄUBER and FRANZ WALDER (D.R.-P. 123375).—Nitroso-compounds are formed when cooled aqueous or slightly acid solutions of *m*-phenylenediamine and its tolyl homologue are rapidly treated with 2 mols. of nitrous acid. These substances are always accompanied by Bismarck-brown which is separated by the addition of sodium chloride, whilst the nitroso-derivatives are isolated by saturating the filtrate with ether and adding sodium carbonate.

Nitroso-*m*-phenylenediamine, $NO{\cdot}C_6H_3(NH_2)_2$ (compare Abstr., 1901, i, 141), crystallises in red, monoclinic plates and melts at 210°; its hydrochloride separates from water in reddish-brown needles.

Nitroso-2 : 4-tolylenediamine, $NO{\cdot}C_6H_2Me(NH_2)_2$, closely resembles its lower homologue and melts at 195°. G. T. M.

Condensation Products from Aromatic *p*-Nitrosoamines and Toluene or Xylene Compounds. By Franz Sachs (D.R.-P. 121745).—2 : 4-*Dinitrobenzylidenedimethyl*-p-*phenylenediamine*, $C_6H_3(NO_2)_2\cdot CH\colon N\cdot C_6H_4\cdot NMe_2$, produced by condensing 2 : 4-dinitrotoluene and nitrosodimethylaniline in boiling alcoholic solution in the presence of a small amount of sodium carbonate or trisodium phosphate, separates from glacial acetic acid as a brownish-violet, crystalline powder with a bronzy lustre; it melts at 196° and is sparingly soluble in the ordinary solvents.

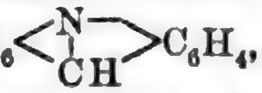
2 : 4 : 6-Trinitrotoluene, 2 : 4 : 6-trinitro-*m*-xylene, and 2-chloro-4-nitrotoluene also yield similar condensation products obtained as dark brown powders. This reaction takes place only when the nitro-compound contains in its molecule at least one other negative radicle, negative results being obtained with *o*- and *p*-nitrotoluene. These condensation products on hydrolysis yield the corresponding benzaldehyde derivatives (compare Abstr., 1901, i, 230). G. T. M.

***m*-Aminotolyloxaminosulphonic Acids.** Schoellkopf, Hartford & Hanna Co. (D.R.-P. 121746).—m-*Aminotolyloxamino-5-sulphonic acid* ("A" acid), $NH_2\cdot C_6H_2Me(NH\cdot CO\cdot CO_2H)\cdot SO_3H$, obtained by heating 2 : 4-tolylenediamine-5-sulphonic acid with a 25 per cent. solution of oxalic acid, separates from the product of reaction in a crystalline form; it yields a sparingly soluble *calcium* salt, a stable *diazo*-compound which is precipitated even from dilute solutions, and a scarlet azo-derivative with R-salt.

The corresponding 2-*aminotolyl*-6-*oxamino*-4-*sulphonic acid* ("B" acid), produced from 2 : 6-tolylenediamine-4-sulphonic acid, yields a soluble *calcium* salt and *diazo*-compound, the azo-derivative with R-salt being orange. G. T. M.

Condensation Products from the Diaminoanthraquinones and Formaldehyde. Badische Anilin- & Soda-Fabrik (D.R.-P. 123745).—1 : 5-, 1 : 3-, and 1 : 8-Diaminoanthraquinones when heated with formaldehyde in methyl or ethyl alcohol, acetone, acetic acid, or carbon disulphide solution yield crystalline condensation products which are insoluble in water, acids, or alkalis, but dissolve in alcohol, giving red solutions. G. T. M.

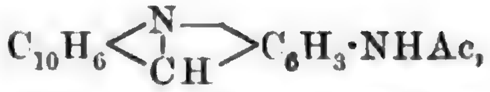
Naphthacridine Derivatives. Carl Ullmann (D.R.-P. 123260. Compare this vol., i, 55, 56).—Phenonaphthacridine,



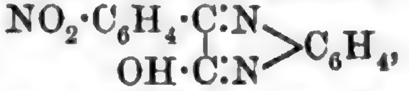
$C_{10}H_6{<}\begin{matrix}N\\|\\CH\end{matrix}{>}C_6H_4$,

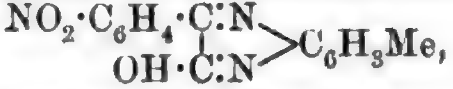
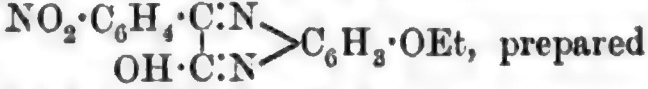
(m. p. 129·5°), is obtained by heating together trioxymethylene, β-naphthol, and aniline at 160°; *o*-tolunaphthacridine, produced in a similar manner from *o*-toluidine, melts at 143°.

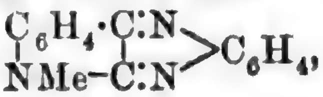
Dimethylphenonaphthacridine, prepared by heating the condensation product of formaldehyde and *m*-xylidine with β-naphthol, crystallises from alcohol or benzene in pale yellow needles and melts at 152°.

Acetylmethylene-p-*phenylenediamine*, $NHAc\cdot C_6H_4\cdot N\colon CH_2$, obtained from acetyl-*p*-phenylenediamine and formaldehyde, forms white crystals melting at 195—200°; when treated with β-naphthol at 150—180°, it yields *acetylaminophenonaphthacridine*,  $C_{10}H_6{<}\genfrac{}{}{0pt}{}{N}{CH}{>}C_6H_3\cdot NHAc$, a compound crystallising from alcohol in yellow needles and melting at 255°. The corresponding *aminophenonaphthacridine*, obtained by hydrolysing the acetyl derivative, crystallises in needles melting at 238°. G. T. M.

1-Phenyl-2:3-dimethyl-5-thiopyrazolone. AUGUST MICHAELIS (D.R.-P. 122287).—1-*Phenyl*-2 : 3-*dimethyl*-5-*thiopyrazolone*, $C_{11}H_{12}N_2S$, obtained by treating the metho-chloride, -bromide, or -iodide of 5-chloro-1-phenyl-3-methylpyrazole, $C_{11}H_{12}N_2Cl_2$, with an alkali sulphide or hydrosulphide, separates from water or alcohol-ether in white crystals and melts at 166°; it forms a crystalline hydrochloride (compare Abstr., 1901, i, 52). G. T. M.

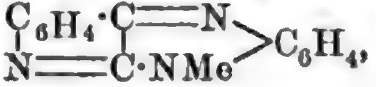
Isatin. By J. BURACZEWSKI and LEON MARCHLEWSKI (*Ber.*, 1901, **34**, 4008—4015. Compare Abstr., 1901, i, 415, 615).—*o*-Nitrobenzoylformic acid condenses with *o*-phenylenediamine hydrochloride in the presence of sodium acetate, forming 2-*hydroxy*-3-o-*nitrophenylquinoxaline*,  $\begin{matrix}NO_2\cdot C_6H_4\cdot C{:}N\\ OH\cdot C{:}N\end{matrix}{>}C_6H_4$, which crystallises in yellowish needles melting at 295° and is soluble in alkalis; its alkaline solution is reduced by ferrous sulphate with the formation of 2-hydroxy-3-*o*-aminophenylquinoxaline; the constitution of the latter compound, which is also obtained from acetylisatin and *o*-phenylenediamine, is therefore confirmed (*loc. cit.*).

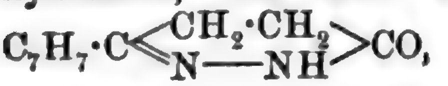
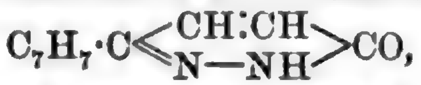
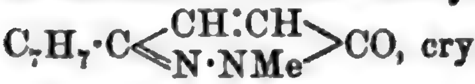
2-*Hydroxy*-3-o-*nitrophenyl*-6-(or 8-)*methylquinoxaline*,  $\begin{matrix}NO_2\cdot C_6H_4\cdot C{:}N\\ OH\cdot C{:}N\end{matrix}{>}C_6H_3Me$, prepared from *o*-tolylenediamine and *o*-nitrobenzoylformic acid, crystallises in yellowish needles melting at 293—294°. 2-*Hydroxy*-6-(or 8-)*ethoxy*-3-o-*nitrophenylquinoxaline*,  $\begin{matrix}NO_2\cdot C_6H_4\cdot C{:}N\\ OH\cdot C{:}N\end{matrix}{>}C_6H_3\cdot OEt$, prepared from ethoxy-*o*-phenylenediamine [NH_2:NH_2:OEt = 1 : 2 : 4] and *o*-nitrobenzoylformic acid, is a yellowish solid melting at 215—216°. 2-*Hydroxy*-3-*phenylquinoxaline*, prepared in an analogous manner, crystallises in pale yellow needles melting at 247°; 2-*Hydroxy*-6-(or 8-)*ethoxy*-3-*phenylquinoxaline*, crystallises in yellow needles melting at 205°. 2-*Hydroxy*-3-o-*aminophenyl*-6-(or 8-)*methylquinoxaline*, which crystallises in dark yellow needles melting at 208—209°, is formed as an acetyl derivative from acetylisatin and *o*-tolylenediamine together with acetylmethylindophenazine; it is separated from the latter by treatment with alkalis, in which the quinoxaline alone dissolves; the acetyl group is eliminated by prolonged boiling of the alkaline solution.

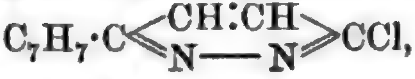
Methyl-*ψ*-isatin and *o*-phenylenediamine condense when heated in acetic acid solution, forming 11-*methylindophenazine*,  $\begin{matrix}C_6H_4\cdot C{:}N\\ NMe-C{:}N\end{matrix}{>}C_6H_4$, (Abstr., 1896, i, 236), which forms yellow crystals melting at 148°, and with concentrated hydrochloric acid gives an orange hydrochloride. This substance is also formed when indophenazine is methylated.

11-*Benzylindophenazine* is obtained from indophenazine and benzyl chloride, and crystallises in orange-yellow needles melting at 171·5°; it is also produced by the condensation of benzyl-ψ-isatin and *o*-phenylenediamine.

With 4-ethoxy-*o*-phenylenediamine, isatin yields a mixture of two ethoxyindophenazines (see Abstr., 1899, i, 719). These can be separated by conversion into the acetyl derivatives and recrystallisation of the latter from alcohol. α-d-*Ethoxyindophenazine* is obtained from the more sparingly soluble acetyl derivative (m. p. 208°) and crystallises in yellow needles melting at 265°; β-d-*ethoxyindophenazine*, obtained from the soluble acetyl derivative (m. p. 165°), is a yellow substance melting at 230°.

Isatin and 3 : 4-diaminobenzoic acid condense to an *indophenazine-7-(or 8-)carboxylic acid*, which is obtained as a crystalline powder melting above 300°; 10-*methyl-ψ-indophenazine*,  $\begin{array}{l} C_6H_4\cdot C{=\!=}N \\ N{=\!=}C\cdot NMe \end{array}{>}C_6H_4$, is prepared from isatin and *o*-aminomethylaniline and crystallises in red needles melting at 175—176°; the *hydrochloride* forms a yellow, crystalline powder. 10-*Phenyl-ψ-indophenazine*, prepared from isatin and *o*-aminodiphenylamine, crystallises in lustrous needles melting at 265—266°. Treatment of these two derivatives of ψ-indophenazine with concentrated acids leads to the formation of indophenazine and not of ψ-indophenazine. K. J. P. O.

p-Tolylpyridazine and its Derivatives. By A. Katzenellenbogen (*Ber.*, 1901, **34**, 3828—3839. Compare Gabriel and Colman, Abstr., 1899, i, 390).—A 71 per cent. yield of β-*p*-toluoylpropionic acid (Abstr., 1888, 951) is obtained when succinic anhydride, toluene, and aluminum chloride are shaken for fifteen hours at the ordinary temperature. When warmed with hydrazine sulphate and sodium hydroxide, the acid is transformed into 3-p-*tolylpyridazinone*,  $C_7H_7\cdot C{<}\begin{array}{c} CH_2\cdot CH_2 \\ N{—}NH \end{array}{>}CO$, which crystallises from alcohol in prisms melting at 155—156°. An acetic acid solution of bromine converts the pyridazinone into 3-p-*tolylpyridazone*,  $C_7H_7\cdot C{<}\begin{array}{c} CH{:}CH \\ N{—}NH \end{array}{>}CO$, which crystallises from acetic acid in hexagonal plates melting at 225°, and is soluble in dilute alkalis, but only sparingly so in ether, alcohol, or benzene. When methylated, it yields 3-p-*tolyl*-1-*methylpyridazone*,  $C_7H_7\cdot C{<}\begin{array}{c} CH{:}CH \\ N\cdot NMe \end{array}{>}CO$, crystallising in colourless needles and melting at 125°. The corresponding *ethyl* derivative melts at 96—97°.

6-*Chloro*-3-p-*tolylpyridazine*,  $C_7H_7\cdot C{<}\begin{array}{c} CH{:}CH \\ N{—}N \end{array}{>}CCl$, obtained by the action of phosphorus oxychloride on the pyridazone, crystallises in pointed prisms, melts at 153°, and is readily soluble in most organic solvents.

6-*Methoxy*-3-p-*tolylpyridazine* crystallises in four-sided plates melting at 114—115°; its *platinichloride* forms golden-yellow crystals melting at 177—179°. The *ethoxy*-derivative crystallises in needles melting at 106°, its *picrate* forms lemon-yellow needles melting at 118°, the *platinichloride* melts and decomposes at 146°, the *aurichloride* softens at 130° and melts at 150—151°, and the *dichromate*,

$$(C_{13}H_{14}ON_2)_2,H_2Cr_2O_7,$$

is an orange-red powder softening at 65° and melting at about 106°. 6-*Phenoxy*-3-p-*tolylpyridazine* forms slender, colourless needles melting at 135°.

6-*Iodo*-3-p-*tolylpyridazine* forms, minute crystals melting at 188°, and when reduced with hydriodic acid and phosphorus yields 3-p-*tolylpyridazine*, which crystallises in glistening, four-sided plates melting at 106—107° and is readily soluble in most organic solvents; the *picrate* crystallises in prisms melting at 151°, the *platinichloride* decomposes at about 125°, and the *aurichloride* softens at 147° and melts at about 198°.

Nitro-3-p-*tolylpyridazine*, $NO_2 \cdot C_7H_6 \cdot C_4N_2H_3$, crystallises in colourless needles melting at 133°; the *picrate* sinters at 170° and melts at about 184°; the *platinichloride* melts and decomposes at 258°, and the *aurichloride* melts at 211—212°.

Amino-3-p-*tolylpyridazine*, obtained by reducing the nitro-compound with stannous chloride, crystallises from water in needles melting at 142—143°, the *picrate* melts and decomposes at 170—171°, the *platinichloride* does not melt at 260°, and the *benzoyl* derivative melts at 178—179°.

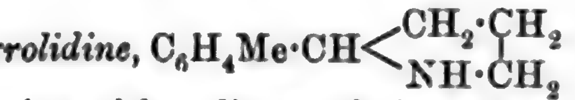
Hydroxy-3-p-*tolylpyridazine* crystallises from alcohol in prisms, and melts at 210—211°; its *hydrochloride* forms colourless needles, the *dichromate*, orange-yellow crystals, and the *platinichloride* pointed prisms melting and decomposing at 175°.

On oxidation with alkaline permanganate, *p*-tolylpyridazine yields *pyridazyl*-3-p-*benzoic acid*, $C_4N_2H_3 \cdot C_6H_4 \cdot CO_2H$, in the form of needles, sparingly soluble in the usual solvents and infusible at 270°.

p-Tolylpyridazine and methyl iodide unite to form a *methiodide*, $C_{12}H_{13}N_2I$, which turns red at 94° and melts at 182—183°.

The *picrate* of the methyl base, $C_{11}H_{10}N_2Me,C_6H_2O_7N_3$, forms lemon-yellow prisms sintering at 174° and melting at 183—184°, and the *platinichloride*, $(C_{11}H_{10}N_2Me)_2PtCl_6$, melts and decomposes at 214—215°.

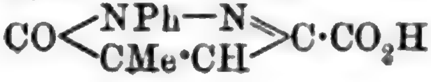
p-*Tolylpyrrolidine*,



$C_6H_4Me \cdot CH<\begin{matrix} CH_2 \cdot CH_2 \\ NH \cdot CH_2 \end{matrix}$, obtained by reducing *p*-tolylpyridazine with sodium and alcohol, is an oil and is volatile with steam; the *picrate* sinters at 145° and melts at 150°; no other salts were obtained in a crystalline state. A further product formed on reduction is 3-p-*tolylhexahydropyridazine*; its *nitrate* forms colourless prisms melting at 186° and the *picrate* melts and decomposes at 167—168°.

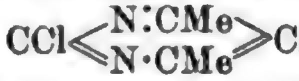
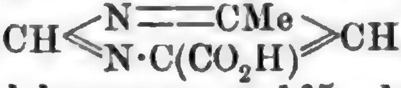
J. J. S.

Action of Hydrochloric Acid on Pyruvic Acid. By A. W. K. de Jong (*Annalen*, 1901, **319**, 121—128. Compare Abstr., 1899, i, 483; 1901, i, 446).—The phenylhydrazone of the $\alpha\gamma$-lactone of α-keto-γ-hydroxybutane-$\alpha\gamma$-dicarboxylic acid, when heated with hydrochloric acid of sp. gr. 1·14 yields 3-keto-2-phenyl-4-methyl-2:3-dihydro-1:2-diazine-6-carboxylic acid,



$$CO<\begin{matrix} NPh-N \\ CMe \cdot CH \end{matrix}>C \cdot CO_2H$$

(compare Rubemann, Abstr., 1894, i, 425). The employment of stronger acid of sp. gr. 1·20 in this experiment leads to the production of the *compound*, $C_{12}H_{10}O_3N_2$, crystallising from glacial acetic acid in white needles and melting at 280°. This substance is insoluble in a solution of alkali carbonate, but dissolves in one of sodium hydroxide; the addition of hydrochloric acid to the alkaline solution causes the precipitation of the monobasic *acid*, $C_{12}H_9O_4N,H_2O$, a compound separating in yellow needles or plates and melting at 237—238°. The new acid forms a readily soluble *potassium* salt and the compound, when boiled with strong hydrochloric acid, regenerates the anhydrous acid, $C_{12}H_9O_4N$, which has the same melting point as its hydrate. Both forms of the acid, when treated with hydrochloric acid of sp. gr. 1·14, yield a compound, crystallising in white needles, which is readily decomposed by water. G. T. M.

4 : 6-Dimethylpyrimidine. By St. Angerstein (*Ber.*, 1901, **34**, 3956—3963. Compare Gabriel and Colman, Abstr., 1899, i, 638).—2-*Chloro*-4 : 6-*dimethylpyrimidine*,  $\mathrm{CCl}{<}\begin{smallmatrix}\mathrm{N{:}CMe}\\ \mathrm{N\cdot CMe}\end{smallmatrix}{>}\mathrm{CH}$, obtained by the action of phosphorus oxychloride on oxydimethylpyrimidine (Abstr., 1894, i, 111), melts at 38°, distils at 223·3° under 756 mm. pressure, dissolves readily in water, alcohol, or ether, and gives a crystalline compound with mercuric chloride. When reduced with zinc dust and water, it yields 4 : 6-dimethylpyrimidine (Gabriel and Colman, *loc. cit.*), which, on oxidation with permanganate, yields *pyrimidine*-4 : 6-*dicarboxylic acid*, crystallising in needles and decomposing at 222°. The acid yields a colourless *hydrochloride*, a yellow *platinichloride*, and a pale green *copper* salt, $C_6H_2O_4N_2Cu$. When less permanganate is employed, 4-*methylpyrimidine*-6-*carboxylic acid*,  $\mathrm{CH}{<}\begin{smallmatrix}\mathrm{N{=\!=}CMe}\\ \mathrm{N\cdot C(CO_2H)}\end{smallmatrix}{>}\mathrm{CH}$, is obtained; it crystallises in needles, melts and decomposes at 165—166°, and is readily soluble in water. The *copper* and *silver* salts have been prepared.

Chlorodimethylpyrimidine readily reacts with an alcoholic solution of sodium methoxide, yielding 2-*methoxy*-4 : 6-*dimethylpyrimidine*, which crystallises in prisms, melts at 35—36°, and distils at 208—209° under 744 mm. pressure. It combines with hydrochloric acid, whilst with mercuric chloride it yields a *compound*,

$$C_7H_{10}ON_2(HgCl_2)_2,$$

which crystallises in needles soluble in hot water or alcohol. 2-*Ethoxy*-4 : 6-*dimethylpyrimidine* is a colourless, strongly refractive oil boiling at 220·1° under 764 mm. pressure; it is appreciably soluble in water, and yields a *compound*, $C_8H_{12}ON_2,HgCl_2$, sparingly soluble in water. The *hydrochloride* is readily soluble and precipitates are not obtained with auric chloride, platinic chloride, potassium dichromate, or sodium picrate. On treatment with bromine water, 5-*bromo*-2-*ethoxy*-4 : 6-*dimethylpyrimidine*, melting at 40—41° and boiling at 254° is obtained.

2-*Phenoxy*-4 : 6-*dimethylpyrimidine* melts at 81°, distils at 305—312°, and is very sparingly soluble in water. With mercuric chloride, it yields the *compound* $C_{12}H_{12}ON_2,2HgCl_2$, crystallising in needles and soluble in alcohol or hot water; the *hydrochloride* is readily soluble in both water and alcohol. 2-*Anilino*-4 : 6-*dimethylpyrimidine* crystallises from toluene in hexagonal plates melting at 88—89° and is insoluble in water; the *platinichloride*, $(C_{12}H_{13}N_3)_2,H_2PtCl_6$, crystallises in yellow needles and the *picrate* in yellow plates melting at 186°. It yields a *nitroso*-derivative, $C_4N_2HMe_2\cdot NPh\cdot NO$, which crystallises in well-developed prisms melting at 130—131°; the *picrate* melts at 184° and the *platinichloride* crystallises in yellow needles.

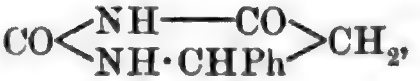
2-*Amino*-4 : 6-*dimethylpyrimidine*, obtained by heating the chloro-base with alcoholic ammonia at 100°, crystallises in needles melting at 150—152°. The *platinichloride* forms yellow prisms melting at 225°. The *hydrochloride* melts at 181° and is readily soluble in alcohol or water. The *picrate* crystallises in yellow plates and melts at 230°, and the *compound* with mercuric chloride, $C_6H_9N_3,HgCl_2$, crystallises in colourless needles.

4 : 6-*Dimethylpyrimidyl* 2-*mercaptan*, $C_4N_2HMe_2\cdot SH$, crystallises in yellow, glistening needles melting at 198° and on oxidation yields 4 : 6-*dimethylpyrimidine* 2-*disulphide*, $S_2(C_4N_2HMe_2)_2$, melting at 162—163° and soluble in acids and in most organic solvents.

J. J. S.

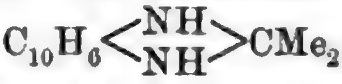
Synthesis of Uracil, Thymine, and Phenyluracil. By EMIL FISCHER and GEORG ROEDER (*Ber.*, 1901, **34**, 3751—3763. Compare Abstr., 1901, i, 294).—*Bromohydrouracil* separates from water or alcohol as a colourless, granular powder; it dissolves in about 5 parts of boiling water or 10 parts of boiling alcohol, but is insoluble in ether or carbon disulphide.

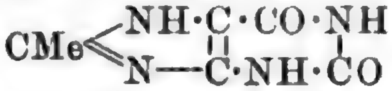
Hydroxyhydrouracil, $C_4H_6O_3N_2$, a substance the constitution of which was not determined, but differs from that of uracil in containing an additional H_2O, is the chief product of the action of alkalis on bromohydrouracil; it dissolves in 12 times its weight of water, crystallises on cooling in colourless, flat needles, and melts at 228° (corr.) with partial decomposition when quickly heated. By heating bromohydrouracil with pyridine, uracil itself $(C_4H_4O_2N_2)$ is formed; it crystallises from hot water in minute, colourless needles, and when quickly heated becomes brown at about 280° and melts with liberation of gas at 335°.

4-*Phenylhydrouracil*,  $\mathrm{CO}<\begin{matrix}\mathrm{NH}{-\!\!-\!\!-}\mathrm{CO}\\ \mathrm{NH\cdot CHPh}\end{matrix}>\mathrm{CH_2}$, prepared from carbamide and cinnamic acid, crystallises from alcohol in prismatic needles, melts at 202—203° (corr.), and dissolves in about 25 parts of hot water or 20 parts of boiling alcohol; it dissolves readily in cold dilute alkalis or in concentrated hydrochloric acid.

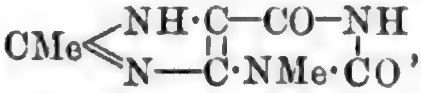
4-*Phenylbromouracil*, $C_{10}H_9O_2N_2Br$, crystallises in minute, pointed needles and melts at about 214° (corr.) with liberation of hydrogen bromide. 4-*Phenyluracil*, $C_{10}H_8O_2N_2$, crystallises in microscopic needles and melts and decomposes at 267° (corr.).

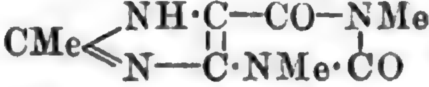
T. M. L.

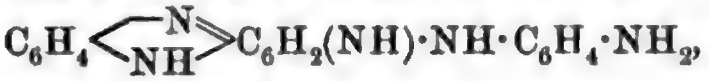
Condensation Products of 1 : 8-Naphthylenediamine and its Derivatives with Acetone. BADISCHE ANILIN- & SODA-FABRIK (D. R.-P. 122475).—1 : 8-Naphthylenediamine sulphate, or the sodium salt of one of its sulphonic acids, readily condenses with acetone in slightly acid solution. The *condensation product* from the diamine itself has the formula  $C_{10}H_6<\begin{matrix}NH\\NH\end{matrix}>CMe_2$; the *substance* $C_{13}H_{14}O_3N_2S$, has also been prepared from 1 : 8-naphthylenediamine-4-sulphonic acid. 1 : 8-Naphthylenediamine-2 : 3-disulphonic acid and 4-chloro-1 : 8-naphthylenediamine give rise to similar derivatives. G. T. M.

Homologues of Xanthine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 121224).—8-*Methylxanthine*,*  $CMe<\begin{matrix}NH\cdot C\cdot CO\cdot NH\\ N{-}C\cdot NH\cdot CO\end{matrix}$, is produced by heating uric acid with acetic anhydride (10 parts) until the insoluble residue no longer reduces ammoniacal silver nitrate; the crude base, purified by conversion into its potassium derivative and reprecipitation with dilute acid, crystallises in colourless prisms or plates which are very sparingly soluble in water and melt above 400°. The *hydrochloride* separates from a concentrated hydrochloric acid solution in colourless, lustrous prisms. The methylxanthine readily dissolves in solutions of ammonia or the alkali hydroxides and yields a stable, gelatinous silver derivative with ammoniacal, and a flocculent double salt with neutral, silver nitrate. The condensation is accelerated either by adding a tertiary base (pyridine, quinoline, or dimethylaniline) or by conducting the operation under pressure at 180—185°.

8-*Ethylxanthine* results when propionic anhydride is employed; this base resembles its lower homologue, but is more soluble in water; it darkens at 350° and decomposes at 390°. 8-iso*Propylxanthine*, prepared in a similar manner from *iso*butyric anhydride, crystallises in short prisms, darkens at 340°, and decomposes at 380°; it is twice as soluble in water as the ethyl compound, but otherwise resembles the latter in dissolving in dilute acids or in solutions of ammonia or the alkali hydroxides, and in yielding a stable silver derivative with ammoniacal silver nitrate.

3 : 8-*Dimethylxanthine*,  $CMe<\begin{matrix}NH\cdot C{-}CO{-}NH\\ N{-}C\cdot NMe\cdot CO\end{matrix}$, obtained by condensing 3-methyluric acid (Abstr., 1900, i, 63) with acetic anhydride in the presence of pyridine, crystallises from water in colourless, felted needles containing $1H_2O$; it darkens at 320° and decomposes at 350°.

1 : 3 : 8-*Trimethylxanthine*,  $CMe<\begin{matrix}NH\cdot C{-}CO{-}NMe\\ N{-}C\cdot NMe\cdot CO\end{matrix}$, derived from 1 : 3-dimethyluric acid, crystallises in needles or prisms, melts at 325°, and is the most soluble of these xanthine derivatives, dissolving in 40 parts of water; with silver nitrate and nitric acid, it yields a crystalline, double salt, and with an ammoniacal solution of the same reagent a gelatinous, silver derivative. G. T. M.

New Synthesis of Fluorindine. By RUDOLF NIETZKI and JOSEF SLABOSZEWICZ (*Ber.*, 1901, **34**, 3727—3732).—5′-*Chloro*-2′ : 4′-*dinitro*-2-*aminodiphenylamine*, $NH_2\cdot C_6H_4\cdot NH\cdot C_6H_2Cl(NO_2)_2$, prepared from o-phenylenediamine and dichlorodinitrobenzene, forms orange-yellow crystals and melts at 232°; o-*diaminodiphenyl*-4 : 6-*dinitro*-1 : 3-*phenylenediamine*, $C_6H_2(NO_2)_2(NH\cdot C_6H_4\cdot NH_2)_2$, crystallises from xylene in glistening, yellow flakes and melts at 253°. *Diaminodiphenyltetraminobenzene*, $C_6H_2(NH_2)_2(NH\cdot C_6H_4\cdot NH_2)_2$, forms a *hydrochloride* and a crystalline double salt with zinc chloride. *Aminophenyldiaminophenazine*,  $C_6H_4\left\langle\begin{matrix}N\\NH\end{matrix}\right\rangle C_6H_2(NH)\cdot NH\cdot C_6H_4\cdot NH_2$, is a brown, crystalline powder and forms a *hydrochloride*.

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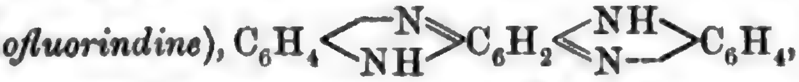
* The positions are numbered in accordance with the scheme proposed by E. Fischer (*Ber.*, 1897, **30**, 557; compare Abstr., 1897, i, 268, line 4, where positions 8 and 9 should be interchanged).

Phenofluorindine (*homofluorindine*),  $C_6H_4\left\langle\begin{matrix}N\\NH\end{matrix}\right\rangle C_6H_2\left\langle\begin{matrix}NH\\N\end{matrix}\right\rangle C_6H_4$, is formed on boiling the preceding compound with dilute hydrogen chloride, and is identical with the substance prepared by Caro.

Dimethylfluorindine (tolufluorindine), prepared from o-tolylenediamine, $[(NH_2)_2{:}Me = 3:4:1]$, was prepared by a similar method, and is perhaps identical with the compound prepared by Föhrenbach (*Diss.*, *Basel*, 1898). T. M. L.

Derivatives of the Phenyl Ethers. By CARL HAEUSSERMANN and OSCAR SCHMIDT (*Ber.* 1901, **34**, 3769—3771).—o-*Azoxyphenyl ether*, obtained by reducing o-nitrophenyl ether dissolved in alcohol containing sodium acetate in the cathode cell with an electric current of 2 amperes and 6 volts, crystallises in yellowish-red leaflets and melts at 95°. p-*Azoxyphenyl ether*, produced in a similar manner from p-nitrophenyl ether, crystallises in orange-yellow needles and melts at 115°. p-*Azoxyphenyl* p-*tolyl ether* from p-nitrophenyl tolyl ether (m. p. 69°) crystallises in lustrous-yellow leaflets and melts at 142°. *Quinol* p-*azoxydiphenyl ether*, from quinol p-nitrodiphenyl ether, obtained by the action of a current of 2 amperes and 25 volts on a dilute alcoholic solution of the nitro-derivative, crystallises, in light yellow leaflets and melts at 183°.

The corresponding amino-derivatives are obtained by the use of a tin cathode (compare Boehringer & Sons, Abstr., 1901, i, 684).

p-*Aminophenyl* p-*tolyl ether*, produced in this way, crystallises from water in white needles and melts at 123°.

p-*Azophenyl* p-*tolyl ether* is prepared by reducing p-nitrophenyl p-tolyl ether with zinc dust and alcoholic potassium hydroxide and oxidising the resulting hydrazo-derivative with atmospheric oxygen; it forms small leaflets melting at 175°. *Quinol* p-*azodiphenyl ether* crystallises from benzene in lustrous, yellowish-red leaflets melting at 210°. G. T. M.

Action of Monochloroacetic Acid on p-Hydroxyazobenzene. By JUL. MAI and FRITZ SCHWABACHER (*Ber.*, 1901, **34**, 3936—3941).—Neither diazobenzene chloride nor p-diazobenzenesulphonic acid react with phenoxyacetic acid; *benzeneazo*-p-*phenoxyacetic acid*,

$$N_2Ph\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H,$$

is, however, obtained by the action of sodium chloroacetate on the sodium derivative of p-hydroxyazobenzene; it crystallises from water in long, yellow needles, melts at 193°, and forms a *sodium* salt insoluble in alcohol and an *ethyl* ester, which is a green, crystalline compound melting at 70°. The corresponding p-*sulphonic acid* was obtained by the action of sodium chloroacetate on phenolazo-*p*-benzenesulphonic acid and forms slightly soluble *potassium sodium*, *potassium hydrogen*, and *barium* salts. The p-*nitro*-derivative, obtained from *p*-nitrobenzeneazophenol, crystallises in lustrous red needles, melts at 205°, and forms a crystalline, violet-coloured *sodium* salt. The phenoxy-acid, when reduced with stannous chloride, yields a *compound* which melts at 225°, forms a soluble *barium* salt, and is probably the semidine, $NH_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2H$; the sodium salt, when similarly reduced, yields a *compound* which crystallises in colourless needles, melts at 239°, forms a slightly soluble, crystalline *barium* salt, and is probably the hydrazo-compound, $NHPh \cdot NH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2H$.

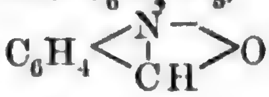
p-Cresolazobenzene, when treated with chloroacetic acid, yields the *compound*, $N_2Ph \cdot C_6H_3Me \cdot O \cdot CH_2 \cdot CO_2H$, which melts at 123°; *p*-tolueneazophenol yields, similarly, the *compound*,

$$C_6H_4Me \cdot N_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2H,$$

which melts at 200°; the dibasic *acid* from *p*-aminobenzoic acid melts at 285° and forms an easily soluble *sodium* salt; the *acid* obtained by treating diphenyltetrazophenol with chloroacetic acid crystallises in brown needles and melts at 255°. R. H. P.

Diphenyl Derivatives. By ERNST BÖRNSTEIN (*Ber.*, 1901, **34**, 3968—3969. Compare Ullmann and Forgan, this vol., i, 89).—When aniline (1 mol.) is diazotised in hydrochloric acid solution and then mixed with a colourless solution of copper sulphate (1 mol.) in sodium thiosulphate (6 mols.), in other words, with cuprous sodium thiosulphate, it yields phenyl sulphide and benzeneazodiphenyl (Griess, *Ber.*, 1876, **9**, 132). *o*- and *p*-Toluidine and sulphanilic acid yield sulphides but not diphenyl derivatives on similar treatment; α-naphthylamine yields α-azonaphthalene. J. J. S.

Reduction, in an Alkaline Solution, of 2 : 4 : 5-Trimethylbenzalazine and the Preparation of some Derivatives of the Reduction Products. By EVERHART P. HARDING (*J. Amer. Chem. Soc.*, 1901, **23**, 829—842).—A more detailed account of work previously published (Abstr., 1900, i, 613—614). E. G.

Conversion of o-Aziminobenzaldehyde into Anthranil. By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1901, **34**, 3874—3877).—When heated with water at 110° for 2 hours, or alone at 120°, *o*-aziminobenzaldehyde, $CHO \cdot C_6H_4 \cdot N_3$, is converted into anthranil, for which the constitution  $C_6H_4\left<\begin{matrix}N-\\ |\\ CH\end{matrix}\right>O$ is suggested; the anthranilic acid formed by the action of alkalis (Abstr., 1901, i, 391), represents a product of further change. Similarly, 3 : 5-dichloro-6-azimino-1-benzaldehyde and 4 : 6-dimethyl-1-azimino-2-benzaldehyde are converted respectively into dichloroanthranil and dimethylanthranil by heating with water. The melting point of dichloroanthranil is 112·5—113·2° (corr.) and not 96—97° (Friedländer and Schreiber, Abstr., 1895, i, 524). T. M. L.

The Present Condition of the Chemistry of Albumin. By Albrecht Kossel (*Ber.*, 1901, **34**, 3214—3245).—A review of the recent advances in the chemistry of albumin, with an extensive bibliography of the subject. G. T. M.

The Present Condition of the Chemistry of Albumin. By Ernst Salkowski (*Ber.*, 1901, **34**, 3884—3885).—A question of priority in relation to Kossel's lecture (preceding abstract). K. J. P. O.

Decomposition of Albumin. By Maximiliano Dennstedt (*Chem. Zeit.*, 1901, **25**, 832—836. Compare Abstr., 1901, i, 780).—It is thought probable that albumoses and peptones are formed simultaneously during the decomposition of proteids. Chittenden's name, *proteoses*, for all proteid-like decomposition products of proteids is suggested as a general term in place of albumose and peptone, whilst, when the source of the proteose is known, special names, for example, caseinose, fibrinose, albumose, &c., are used. The method of formation can also be indicated by prefixes such as pepto-, trypto-, bacteri-, acid-, alkali-, &c. When wheat fibrin or zein is boiled with baryta water, part of the nitrogen of the proteid is evolved as ammonia and part of the sulphur converted into barium sulphide or sulphate. From wheat fibrin, five distinct proteoses have been isolated and analysed. They all have strong acidic properties and may be titrated by the aid of standard alkali; the results vary, however, with the indicator employed, and they are all probably polybasic acids. Two definite products have been obtained from zein, and these also have acid properties. When zein is heated with water at pressures below 0·22 atmosphere, it is transformed into an insoluble modification having the same composition. As the pressure is increased, ammonia and hydrogen sulphide are formed, together with proteoses which have acidic properties and are present as ammonium salts in the final product. Three of these proteoses have been obtained and analysed; they appear to be more nearly allied to zein than the proteoses obtained by the aid of baryta water, and all give the Millon and biuret reactions.

It is thought that the formation of proteoses from proteids is not merely a hydrolytic action, but is a complex chemical decomposition accompanied by loss of nitrogen and sulphur; water is taken up, and oxidation probably occurs. J. J. S.

Nature of Enzymes. By Thomas Bokorny (*Chem. Centr.*, 1901, ii, 1210; from *Pharm. Centralhalle*, **42**, 681—684).—The similarity of the behaviour of the enzymes to that of protoplasm indicates that the former substances are active albumins (protoplasmaproteïn) belonging to the group of nucleoalbumins. The original paper contains a table in which descriptions of the properties of these substances are placed side by side. The enzymes are contained in, and secreted by, the living protoplast, and can be regenerated in the necessary quantity. E. W. W.

Organic Chemistry.

Law governing the Formation of Additive Products and their subsequent Decomposition. By Arthur Michael [with T. H. Mighill] (*Ber.*, 1901, **34**, 4215—4226).—Comparative experiments on the elimination of bromine by means of zinc from the bromides of various unsaturated compounds show the general applicability of the law that, in a series of isomeric or homologous additive products, those which are formed the most readily are also those which are most readily decomposed. In the case of the dibromides of the series ethylene to *iso*butylene, the amount of bromine which zinc eliminates increases as the series is ascended. Experiments with the isomeric ethyl dibromosuccinates, ethyl dibromomethylsuccinates, and methyl $\alpha\beta$-dibromocrotonates are also described. Of the two isomeric β-bromocinnamic acids, the one with the higher melting point is the more readily converted into phenylpropiolic acid.

The *methyl* ester of the $\alpha\beta$-dibromocrotonic acid, which melts at 94°, is a colourless liquid which boils at 94° under 11 mm. pressure; the *methyl* ester of the isomeric acid (m. p. 120°) is a colourless liquid which boils at 102—104° under 14 mm. pressure. R. H. P.

Fluorobromo-derivatives containing Two Atoms of Carbon. IV. By Frédéric Swarts (*Bull. Acad. Roy. Belg.*, 1901, **7**, 383—414. Compare Abstr., 1898, i, 457; 1899, i, 254).—*Difluorobromoethane*, $CHF_2\cdot CH_2Br$, obtained in theoretical quantity by heating together, at 100°, 2 mols. of antimony trifluoride and 3 mols. of tribromoethane, is a colourless, very volatile liquid with an agreeable ethereal odour; it has a sp. gr. 1·82443 at 18·5°, and 1·83685 at 10·5°; n_α 1·39300, n_D 1·39400, and n_H 1·4047 at 10·5°. It is only slightly soluble in water, and mixes in all proportions with organic solvents. When cooled in liquid air, it solidifies to a crystalline mass which melts at −74·5°. It is not acted on by oxidising agents. When heated at 180° with bromine and ferric bromide, it yields tetrabromoethane, and when reduced with zinc in sodium hydroxide solution yields fluoroethylene. *Fluoroethylene*, C_2H_3F, is a colourless, odourless gas, which does not solidify when cooled in liquid air and is insoluble in water, but alcohol dissolves four times, and acetone 5·5 times its own volume of the gas at 20°. It burns in air with a green edged flame. It is readily absorbed by bromine, fluorodibromoethane being formed. *Fluorodibromoethane*, $CHFBr\cdot CH_2Br$, boils at 121·5°, has a sp. gr. 2·26333 at 10·5°, and n_α 1·51235, n_D 1·51759, and n_H 1·53278 at 10·5°. It crystallises at −55°, and melts at −54°.

When difluorobromoethane is heated with potassium hydroxide dissolved in ethyl alcohol, it yields difluorodiethyl ether and difluoroethylene. The yield of difluoroethylene in this case is 32 per cent. of the theoretical; if methyl alcohol is employed instead of ethyl alcohol, then the yield is 26 per cent., whereas with propyl alcohol it is 40 per cent., and with amyl alcohol 61 per cent. In all cases, the corresponding difluoroether is also produced.

Difluoroethylene, $CF_2:CH_2$, is a colourless, odourless gas of density 2·21, corresponding with a mol. wt. of 63·84, the calculated mol. wt. being 63·9. Alcohol or chloroform dissolves 1½ times its own volume of the gas. It neither polymerises nor oxidises when exposed to the air, and when cooled in liquid air, it solidifies to snow-like flakes. It readily absorbs bromine, *a-difluorodibromoethane* being formed.

a-Difluorodibromoethane, $CF_2Br{\cdot}CH_2Br$, is a colourless liquid, boils at 93°, has a sp. gr. 2·4228 at 12·2°, n^{a} 1·44957, n_D 1·45249, n_H 1·46555 at 12·2°; it solidifies at – 58° and melts at 56·5°.

Difluorodiethyl ether, $CHF_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$, is a very volatile, colourless liquid with an ethereal odour, is somewhat soluble in water, and has a sp. gr. 1·039 at 15°. It is oxidised by nitric acid or chromic mixture.

Difluoroethyl methyl ether, $CHF_2{\cdot}CH_2{\cdot}O{\cdot}CH_3$, boils at 47°; 100 vols. of water dissolve 5 vols. of this compound. On oxidation with chromic mixture, it yields *difluoroacetic acid*. *Barium difluoroacetate* is very soluble in water, but almost insoluble in alcohol. It crystallises in star-like aggregates of slender needles.

Difluoroethyl propyl ether boils at 89°.

Since difluoroethyl methyl ether on oxidation gives difluoroacetic acid, it follows that it must contain the group $CHF_2{\cdot}CH_2$–, which must also be present in the difluorodiethyl ether.

Difluoroiodoethane, $C_2H_3IF_2$, produced by heating difluorobromoethane with calcium iodide in alcoholic solution, is a colourless liquid, boils at 89·5°, has a sp. gr. 2·24328 at 12·2°, and n_a 1·46455, n_D 1·46807, and n 1·48467 at 12·2°. When oxidised with nitric acid, it yields difluoroacetic acid.

When tribromoethane is treated with a mixture of antimony trifluoride and bromine, both difluorobromoethane and fluorodibromoethane are produced. The fluorodibromoethane thus produced is in every way identical with that obtained by the action of bromine on fluoroethylene.

Fluorobromoethylene, $CH_2:CBrF$, is obtained by the action of a mixture of potassium acetate and carbonate on fluorodibromoethane. It is a very volatile liquid boiling at 30—33°, and readily polymerises and oxidises on exposure to air (compare fluorobromoethylene, $CHBr:CHF$, *Bull. Acad. Roy. Belg.*, 1897, [iii], **33**, 456). H. R. Le S.

Action of Normal Propyl and Butyl Alcohols on their respective Sodium Derivatives; Synthesis of Dipropyl and Dibutyl Alcohols. By Marcel Guerbet (*Compt. rend.*, 1901, **133**, 1220—1222. Compare Abstr., 1899, i, 471, 472; 1901, i, 182, 307, 625).—When propyl alcohol is heated under pressure for 24 hours at 220—230°, sodium propionate, propyl propionate, and a hexylic alcohol are formed; much hydrogen is produced during the operation. The hexylic alcohol is β-methylamyl alcohol (b. p. 148°) being oxidised by chromic acid to β-methylvaleric acid (b. p. 193·5°).

Under the same conditions, butyl alcohol yields corresponding products; the *octylic alcohol* (dibutyl alcohol), $C_8H_{17}{\cdot}OH$, obtained is a colourless, oily liquid boiling at 181° under 758 mm. pressure, and has a sp. gr. 0·8483 at 0°. K. J. P. O.

Preparation of Trichloro*tert.*butyl Alcohol. By Marcel Guédras (*Compt. rend.*, 1901, **133**, 1011).—If a mixture of equal volumes of acetone and chloroform is allowed to drop on potassium hydroxide heated at 30°, and the mixture is afterwards heated at 50° for an hour, *trichloro*tert.*butyl alcohol*, $CCl_3\cdot CMe_2\cdot OH$, is formed, and can be isolated by distilling in steam, after removal of unaltered acetone and chloroform by heating at a temperature below 70°. It melts at 80—81°, boils at 167°, has a characteristic camphoraceous odour, is almost insoluble in cold water, but soluble in most organic solvents, and is not affected by dilute acids or alkalis. It produces local anæsthesia and has antiseptic properties. C. H. B.

Fermentation Amyl Alcohol. By Gustave Bemont (*Compt. rend.*, 1901, **133**, 1222—1224).—A specimen of the amyl alcohol, obtained by repeated fractionation of commercial fusel oil, and representing one-third of the quantity of the latter, boiled at 131—131·5°, has a sp. gr. 0·8065 at 16° and $[\alpha]_D$ −0°55·5′. On oxidation with chromic acid, it yields an active valeric acid which boils at 175° under 763 mm. pressure and has $[\alpha]_D$ +2°31·3′. The alcohol is probably *a*-methylbutyl alcohol, and the acid *a*-methylbutyric acid. In the oxidation are also formed a valeraldehyde, which boils at 92—93° under 761 mm. pressure and has $[\alpha]_D$ +0°22·7′, and an amyl valerate boiling at 191—192° under 743 mm. pressure, and having $[\alpha]_D$ 3°14·8′. K. J. P. O.

Synthesis and Properties of *l*-Erythritol. By Léon Maquenne (*Ann. Chim. Phys.*, 1901, **24**, [vii], 399—412).—A *résumé* of work already published (compare Abstr., 1900, i, 423, 472; 1901, i, 497). G. T. M.

Esterification of Phosphorous Acid by Glycerol and Glycol. By P. Carré (*Compt. rend.*, 1901, **133**, 882—884).—A *glycerophosphorous acid* having the formula $O{:}PH(OH)\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ is obtained on warming glycerol with phosphorous acid; the second hydroxyl group of the acid is not esterified even when the alcohol is in excess. The limits of esterification with molecular proportions, at 125° under the ordinary pressure, is reached in 20—30 hours, 60·6 per cent. of the acid being converted into ester; prolonged heating lowers the percentage owing to the loss of glycerol by evaporation. The limit is reached more rapidly when the experiment is made at 125° under 15 mm. pressure, the time required being 10 hours.

Barium glycerophosphite, $Ba(C_3H_9O_5P)_2$, is amorphous and very soluble; it is hydrolysed by boiling water and by cold solutions of the alkali hydroxides.

The *acid*, $O{:}PH(OH)\cdot CH_2\cdot CH_2\cdot OH$, results from the interaction of glycol and phosphorous acid; it is monobasic, its deliquescent barium salt having the composition $Ba(C_2H_6O_4P)_2$. G. T. M.

New Volatile Beryllium Salt. By G. URBAIN and H. LACOMBE (*Compt. rend.*, 1901, **133**, 874—876).—The basic *beryllium acetate*, $Be_4O(OAc)_6$, produced by dissolving the product of the action of dilute acetic acid on beryllium hydroxide in glacial acetic acid, separates from this solvent in needles or octahedral crystals insoluble in cold water and almost insoluble in alcohol or ether; it is decomposed by hot water. The salt crystallises best from chloroform, melts to a colourless liquid at 283—284°, and boils without decomposition at 330—331° under the ordinary pressure. The vapour may be superheated to 360° without undergoing any decomposition. The salt may even be heated at 150° in the presence of hydrochloric and glacial acetic acids without alteration. The vapour density of the compound determined by V. Meyer's method is additional evidence in favour of the bivalent character of beryllium. G. T. M.

Action of higher Aliphatic Acids on Normal Alkali Carbonates. By J. KLIMONT (*J. pr. Chem.*, 1901, [ii], **64**, 493—495).—The higher fatty acids (stearic, oleic, arachic) which are insoluble in water react with aqueous sodium carbonate, giving sodium hydrogen carbonate and the sodium salt of the fatty acid. With lower acids, which are somewhat soluble (decoic, &c.), the sodium hydrogen carbonate is also decomposed. K. J. P. O.

Action of Ethyl Sodiomalonate on Tribromides. By WLADIMIR N. IPATIEFF and SWIDERSKI (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 532—540).—By the action of bromine, dimethylethylcarbinol yields a mixture of two dibromo-compounds, $CMe_2Br\cdot CHMeBr$ and $CH_2Br\cdot CMeBr\cdot CH_2Me$, which, when further brominated, give two isomeric tribromo*iso*pentanes of the constitution $CMe_2Br\cdot CHBr\cdot CH_2Br$ and $CH_2Br\cdot CMeBr\cdot CHMeBr$. On treating the mixed tribromo-derivatives (1 mol.) with three atomic proportions of sodium and ethyl malonate (3 mols.), the following compounds were obtained: (1) ethyl ethanetetracarboxylate; (2) the *ethyl* ester of an unsaturated *acid* of the composition $C_8H_{12}O_4$ and probably of the constitution

$$CHMe\!:\!CMe\cdot CH_2\cdot CH(CO_2H)_2;$$

two fractions of the ethyl ester, boiling under 10 mm. pressure at 115—120° and 120—124°, have respectively the sp. gr. 1·058 and 1·064 at 0°/0°; (3) the ethyl ester of an unsaturated *bromo*-acid, $CMeBr\!:\!CMe\cdot CH_2\cdot CH(CO_2H)_2$, which, after crystallisation from benzene, melts at 115—117°; (4) an ester isomeric with (3) and corresponding with an *acid*, $CMe_2\!:\!CBr\cdot CH_2\cdot CH(CO_2H)_2$, melting at 157—158°. Both these bromo-acids form insoluble *silver* and *calcium* salts. T. H. P.

Isoprenic Acid. By WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 540—545).—The action of sodium ethoxide on dibromoisoprene and ethyl malonate gives rise to an *ethyl* ester, $C_{12}H_{18}O_4$, which in an impure condition boils at 125—128° under 15 mm. pressure; it is a transparent liquid having a faint odour and combines with bromine, and decolorises 1 per cent. permanganate solution; it has a sp. gr. 1·0566 at 0°/0° and n_D 1·45041, the molecular refraction calculated from this number showing that the molecule contains one double linking. On hydrolysis, the ester yields iso*propenyltrimethylenedicarboxylic acid* (*isoprenic acid*), $CH_2{:}CMe\cdot CH\left<\begin{matrix}CH_2\\ | \\ C(CO_2H)_2\end{matrix}\right.$, which was obtained as an amorphous powder soluble in water or acetic acid; in freezing aqueous solution, the values 245, 233, and 314 were obtained for the molecular weight, so that the acid undergoes polymerisation; the acid melts and decomposes at about 115°, decolorises permanganate solution, and combines with bromine and hydrogen bromide, giving compounds not readily purified. The salts of the acid are mostly insoluble in water and amorphous; the *calcium* salt, $C_8H_8O_4Ca,2H_2O$, is obtained as a white, amorphous precipitate.

The composition of dibromoisoprene is probably

$CH_2{:}CMe\cdot CHBr\cdot CH_2Br$. T. H. P.

Cystin. By JULIUS MAUTHNER (*Zeit. Biol.*, 1901, **42**, 176—186).—Certain metallic compounds of cystin are described, particular attention being directed to that with copper, which is crystalline and has the formula $C_6H_{10}O_4N_2S_2Cu$. Cystin also forms a crystalline compound with hydrogen chloride, $C_6H_{12}O_4N_2S_2,2HCl$. Compounds are also described of the formulæ $C_6H_8O_4N_2S_2Hg_2,HgCl_2$;

$2C_6H_{10}O_4N_2S_2Hg,HgCl_2,7H_2O$; $2C_6H_8O_4N_2S_2Hg_2,Hg(NO_3)_2$;

Baumann (*Zeit. physiol. Chem.*, **8**, 300) showed that cystin may be reduced to cystein by tin and hydrochloric acid and subsequent removal of the tin by hydrogen sulphide. It is now shown that hydrogen sulphide alone will bring about the same reduction.

W. D. H.

Action of Fuming Sulphuric Acid on Acetaldehyde, Propaldehyde, and Acetone. By MARCEL DELÉPINE (*Compt. rend.*, 1901, **133**, 876—878).—The vapour of acetaldehyde, when passed into fuming sulphuric acid (50 per cent. SO_3), yields acetaldehyde-ββ-disulphonic acid, $CHO\cdot CH(SO_3H)_2$, and methanedisulphonic acid. The former acid yields, with aniline, *p*-toluidine and the naphthylamines, *compounds* of the type $CH(SO_3H)_2\cdot CH{:}NR,2H_2O$.

Propaldehyde, under these conditions, gives rise to propaldehyde-ββ-disulphonic acid, $CHO\cdot CMe(SO_3H)_2$, the potassium salt of which, when heated with barium hydroxide solution, yields the corresponding salts of formic and ethylidenedisulphonic acids.

Acetone also undergoes sulphonation, yielding *acetone-αγγ-trisulphonic acid*, $SO_3H\cdot CH_2\cdot CO\cdot CH(SO_3H)_2$, and the products of its hydrolysis, namely, disulphoacetic and methanedisulphonic acids. These acids were identified as barium salts. *Barium acetone-αγγ-trisulphonate*, $Ba_3[C_3H_3O(SO_3)_3]_2,2H_2O$, when dried at 105°, is an amorphous substance resembling alumina or silica; it yields the corresponding salts of disulphoacetic and methanedisulphonic acids when boiled with barium hydroxide solution. G. T. M.

Electrolytic Production of Haloid Derivatives of Acetone. By A. RICHARD (*Compt. rend.*, 1901, **133**, 878—880).—Monochloroacetone is produced by electrolysing a mixture of hydrochloric acid and acetone. The best yield is obtained when the acetone is in excess and the electrolysis conducted in a well-cooled electrolytic cell fitted with an anode having a large surface. The hydrogen evolved at the cathode has no action on the product.

Monobromoacetone is conveniently prepared by electrolysing a mixture of hydrobromic acid and acetone at 35—40°, but in this case the hydrogen must be evolved in a separate cathode cell, owing to its reducing action on the product. G T. M.

Action of Nitric Acid on Aliphatic Compounds containing the Group CH(OH). I. Action of Nitric Acid on Secondary Alcohols. II. Action of Nitric Acid on Ketonic Alcohols, R·CO·CH(OH)·R.

By Giacomo Ponzio (*Atti R. Accad. Sci. Torino*, 1900—1901, **36**, 721—733).—The first part of this paper has been already abstracted (see Abstr., 1901, i, 477).

The action of nitric acid of sp. gr. 1·37 on ketonic alcohols, R·CO·CHR·OH (α-ketoles or aliphatic benzoins), affords a convenient means of preparing symmetrical α-diketones of the aliphatic series. The following compounds have been obtained in this way.

Dipropionyl, prepared from propioin, [$CH_2Me\cdot CO\cdot CH(OH)\cdot CH_2Me$], was distilled in a current of steam and converted into its *dioxime*, $C_6H_{12}O_2N_2$; this crystallises from benzene in shining, white needles which melt and sublime at 185°, and are soluble in water, alcohol, chloroform, ether, or light petroleum.

Dibutyryl, $CH_2Et\cdot CO\cdot CO\cdot CH_2Et$, obtained together with dinitropropane by the oxidation of butyroin, is a yellow oil. The *dioxime*, $C_8H_{16}O_2N_2$, separates from benzene in slender, shining needles melting at 175°, and dissolving in alcohol, ether, or chloroform.

Diisobutyryl, $CHMe_2\cdot CO\cdot CO\cdot CHMe_2$, obtained from *iso*butyroin, gives a *dioxime*, $C_8H_{16}O_2N_2$, which crystallises from benzene in white needles melting and subliming at 163—164° and dissolving in alcohol or ether.

Diisovaleryl, $CHMe_2\cdot CH_2\cdot CO\cdot CO\cdot CH_2\cdot CHMe_2$, prepared from *iso*valeroin, yields a *dioxime*, $C_{10}H_{20}O_2N_2$, separating from benzene in shining, white needles which melt and sublime at 195°; it is soluble in alcohol, ether, or chloroform. T. H. P.

Synthetical Experiments with Tetra-acetylchlorodextrose and Tetra-acetylchlorogalactose.

By Zdenko H. Skraup and R. Kremann (*Monatsh.*, 1901, **22**, 1037—1048).—Investigation of the action of phenylhydrazine on tetra-acetylchlorodextrose has resulted in the isolation of glucosazone only, in addition to acetylphenylhydrazine and phenylhydrazine hydrochloride.

Attempts to synthesise a disaccharide by the action of tetra-acetylchlorodextrose on the sodium and lead derivatives of dextrose were unsuccessful. A small amount of β-penta-acetyldextrose (m. p. 112°) was formed from tetra-acetylchlorodextrose on boiling it with molecular silver in toluene. When heated with metallic sodium and finely divided silver nitrate in ether, tetra-acetylchlorodextrose was converted into *tetra-acetylnitrodextrose* which melted at 92°. This, when heated with sodium acetate and glacial acetic acid, yielded α-penta-acetyldextrose (m. p. 132°). On recrystallisation from alcohol, the almost inactive tetra-acetylnitrodextrose ([α]$_D$ +1·536°) became active ([α]$_D$ +143·65° at 25°) and melted at 145°. This is probably the tetra-acetylnitrodextrose previously described by Colley and Königs (m. p. 151°; [α]$_D$ +149·16° at 18°).

When boiled with metallic sodium and silver nitrate, in ether, tetra-acetylchlorogalactose exchanges the chlorine atom for hydroxyl, yielding *tetra-acetylgalactose*. This melts at 145°, and has [α]$_D$ +137·17° at 25°. When boiled with sodium acetate and acetic anhydride, it is converted into penta-acetylgalactose (m. p. 142°). By hydrolysis of the tetra-acetylgalactose and subsequent treatment with phenylhydrazine, glucosazone was obtained. G. Y.

Hepta-acetylmaltose Nitrate (Acetonitromaltose) and Hepta-acetyl-β-methylmaltoside. By WILHELM KOENIGS and EDUARD KNORR (*Ber.*, 1901, **34**, 4343—4348. Compare Abstr., 1901, i, 369). —*Hepta-acetylmaltose nitrate*, $C_{12}H_{14}O_3(OAc)_7 \cdot NO_3$, is prepared by treating octoacetylmaltose with an ice-cold mixture of chloroform and fuming nitric acid; it crystallises in large prisms melting at 93—95° and has [α]$_D$ +149°18′ at 19°. On boiling the nitrate with methyl alcohol in the presence of barium carbonate and a few drops of pyridine, hepta-acetylmethylmaltoside is formed; this melts at 128—129°, and has [α]$_D$ +60°46′ at 20° (compare Fischer and Armstrong, Abstr., 1901, i, 671). On hydrolysis with barium hydroxide, β-methylmaltoside is obtained, forming colourless needles melting at 93—95° and decomposing at 100°; fermentation converted it into β-methylglucoside.

Pure octoacetylsucrose can be quantitatively hydrolysed when it is treated with a cold solution of sodium hydroxide in aqueous methyl alcohol for a few hours. K. J. P. O.

Cellobiose. By ZDENKO H. SKRAUP and J. KÖNIG (*Monatsh.*, 1901, **22**, 1011—1036. See Abstr., 1901, i, 370).—The name *cellobiose* is now used for the substance previously termed cellose. Cellobiose, on hydrolysis by dilute sulphuric acid, is shown to yield dextrose only. Cellobiose forms a *phenylhydrazone* which decomposes at 90° and an *osazone* which melts at 198°.

Hepta-acetylchlorocellobiose, $C_{26}H_{35}O_{18}Cl$, is formed by the action of hydrogen chloride on the solution of heptacetylcellobiose in acetic anhydride. It forms small needles which melt at 178°.

Hepta-acetylmethylcellobioside is formed by shaking with silver carbonate hepta-acetylchlorocellobiose in methyl alcohol solution; it crystallises from alcohol in white needles melting at 173°, and on hydrolysis yields a substance which closely resembles cellobiose but may be methylcellobioside.

Attempts to obtain cellobiose from sprouting beans were unsuccessful. G. Y.

Acetylation of Soluble Starch. By FRITZ PREGL (*Monatsh.*, 1901, **22**, 1049—1066).—Soluble starch prepared by Zulkowsky's method yielded, on acetylation by acetic anhydride in presence of a small quantity of sulphuric acid in the cold, an amorphous *triacetyl* derivative, $C_6H_7O_5Ac_3$, which did not reduce copper or bismuth salts, and was not coloured by iodine. It sintered at 260°, decomposed at 275°, and had $[\alpha]_D$ 163·6°. Molecular weight determinations showed the molecular weight to be from eight to nine times that corresponding with the empirical formula. The product obtained on hydrolysis of the acetyl derivative was identical with the soluble starch and had $[\alpha]_D$ +191·73° at 20°. Soluble starch had $[\alpha]_D$ +191·27° at 20°. On analysis, both gave the formula $C_6H_{10}O_5$ (compare Syniewski, Abstr., 1898, i, 61).

Acetylation with an increased amount of sulphuric acid yielded a product having the empirical formula $C_6H_7O_5Ac_3$; the molecular weight determinations showed, however, that this formula must be tripled. This acetyl compound is soluble in alcohol, melts at 150—155°, has $[\alpha]_D$ 149·03°, and reduces alkaline copper solutions. Hydrolysis yielded a dextrin which gave a red coloration with iodine, had $[\alpha]_D$ +187·0°, and could not be identified with any dextrin previously described.

G. Y.

Humic Substances. By FAUSTO SESTINI (*L'Orosi*, 1901, **24**, 289—299).—The humic substances which have been previously described by various authors must not be considered as so many different modifications of one individual substance, since facts are not lacking which indicate marked differences in properties between humic substances from divers sources. Artificial humic matter prepared from non-nitrogenous compounds contains no trace of nitrogen, whilst that obtained from the humus of the soil retains tenaciously a certain quantity of nitrogenous material. The author applies Liebermann's theory of colour shade (Abstr., 1901, ii, 368) to the change of colour from black to red and afterwards to yellow when humic substances are oxidised and nitrated; also to the case of sacculmic acid which changes from brown to yellow when a portion of its hydroxyl is replaced by bromine, whilst the black colour returns if the hydroxyl is restored to the compound. The influence of the methoxy-group on the colour of organic compounds, which was pointed out by Liebermann (*loc. cit.*), is probably exerted in the case of humic substances, the author having often detected an odour of chloroform, bromoform, or methyl esters on treating such substances with chlorine or bromine. By oxidation and nitration with concentrated nitric acid (sp. gr. 1·4), the molecule of humic substances is quickly destroyed with the formation of a mixture of products among which are nitration products belonging to the aromatic series; the only aromatic group which has been identified is the benzene nucleus. Quinone readily undergoes change into a black mass, which is also formed at the ordinary temperature from an aqueous solution of quinone kept in the dark and in an atmosphere of carbon dioxide; it is probable that an additive product of quinone with water is first formed, and that this is gradually decomposed between 15° and 95° into quinol and black matter by the action of the liberated oxygen. The author confirms the views previously put forward by him that ulmin and sacculmin cannot be regarded as merely mixtures of the potassium salts of humic acids. As regards the chemical functions of humic substances, it is probable that beside anhydride or ether-linkings they contain ketonic, hydroxyl, and alkyl groups, partly arranged in open, and partly in closed, chains.

T. H. P.

Birotation of Chitosamine (Glucosamine). By ERNST EDW. SUNDVIK (*Zeit. physiol. Chem.*, 1901, **34**, 157).—At a low temperature, a solution of glucosamine hydrochloride shows a rotation of 24·5°. After heating for an hour and then cooling to the same temperature, the rotation is only 18°. W. D. H.

Action of Monoamino-acids on Phosphotungstic Acid. By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1901, **33**, 574—578. Compare Kossel and Kutscher, Abstr., 1901, i, 107). —A solution of pure phosphotungstic acid does not precipitate glycine, leucine, aminovaleric acid, or tyrosine from 5 per cent. solutions. Phenylaniline is, however, partially or wholly precipitated. It is probable that in the presence of other substances the amino-acids may be precipitated. The precipitates obtained in the investigation on histone bases (this vol., i, 193) gave negative results when tested for amino-acids. J. J. S.

Action of Dilute Mineral Acids on Ethyl Aminodimethyl Acrylate. By LOUIS BOUVEAULT and A. WAHL (*Bull. Soc. Chim.*, 1901, [iii], **25**, 1031—1040).—When heated with dilute mineral acids, ethyl aminodimethylacrylate, $CMe_2\text{:}C(NH_2)\cdot CO_2Et$, is converted into *ethyl dimethylpyruvate*, $CHMe_2\cdot CO\cdot CO_2Et$, which forms a mobile, colourless, ethereal liquid and boils at 64—69° under 35 mm. or at 60° under 10 mm. pressure. The *semicarbazone*,

$$CHMe_2\cdot C(CO_2Et)\text{:}N\cdot NH\cdot CO\cdot NH_2,$$

separates in needles from a mixture of ether and light petroleum and melts at 95—96°. The *oxime*, $CHMe_2\cdot C(CO_2Et)\text{:}NOH$, crystallises in needles from a mixture of ether and light petroleum and melts at 57°.

Dimethylpyruvic acid, $CHMe_2\cdot CO\cdot CO_2H$, distils at 65—67° under 10 mm. pressure, forms colourless leaflets, and melts at 31°; its *oxime* forms white crystals and melts and decomposes at 163—165°; the *phenylhydrazone* separates from aqueous methyl alcohol in yellow needles often several centimetres long, and melts at 156—157° without decomposition. The acid is reduced by sodium amalgam and alcohol to α-hydroxy*iso*valeric acid; by the action of ammonia on the ester, dimethylpyruvamide (Moritz, Trans., 1880, **35**, 14) is produced. Dimethylpyruvic acid has been prepared in an impure state by Moritz (*loc. cit.*), by Brunner (Abstr., 1895, i, 335), who describes a silver salt and a diphenylhydrazone melting at 129°, and by Kohn (Abstr., 1899, i, 328), who describes an oxime melting at 102° and a phenylhydrazone melting at 137°, but the products obtained differ substantially from those here described. T. M. L.

Thiocyanogen, the so-called ψ-Thiocyanogen, and the Yellow Colouring Matter obtained from Thiocyanates. By ALWIN GOLDBERG (*J. pr. Chem.*, 1901, [ii], **64**, 439—470. Compare Abstr., 1901, i, 516, 677).—Analyses of commercial canarin show that it has the formula $C_8H_6ON_8S_7$ (*loc. cit.*). The decomposition of canarin by water, alkalis, concentrated acids, and heat is studied. Metallic compounds with sodium, potassium, copper, zinc, silver, and magnesium are described.

The yellow substance which is formed as a bye-product in the preparation of the dye canarin is contained in the mother liquors, from which the sodium salt of canarin has separated, and has the formula $C_3H_4ON_4S_2$ (?). The relation of the yellow substance to canarin is discussed, and constitutional formulæ are suggested for both substances. K. J. P. O.

New Methods for the Preparation of Dithiocyanochromium Salts. By Paul Pfeiffer (*Ber.*, 1901, **34**, 4303—4307. Compare Abstr., 1900, i, 688).—Dithiocyanodiethylenediaminechromium thiocyanate (*loc. cit.*) may be obtained when potassium chromothiocyanate, $K_3CrS_6C_6N_6$, is heated with anhydrous ethylenediamine for three hours on the water-bath. The yield is small as part undergoes decomposition during purification by crystallisation from water. When this salt is heated with ethylenediamine, it is partially transformed into the luteo-salt, $Cr(C_2H_8N_2)_3(SCN)_3$, as also is potassium chromothiocyanate. J. J. S.

Chromammonium Compounds. II. By Paul Pfeiffer (*Zeit. anorg. Chem.*, 1901, **29**, 107—137. Compare Abstr., 1900, i, 559; 1901, ii, 659).—*Dithiocyanodiethylenediaminechromium salts.* Dithiocyanodiethylenediaminechromium thiocyanate,

$$[Cr(C_2H_8N_2)_2(SCN)_2]SCN,xH_2O,$$

was obtained in prismatic needles from the salt $[Cr(C_2H_8N_2)_3]Cl_3$ by first preparing the luteothiocyanate $[Cr(C_2H_8N_2)_3](SCN)_3,H_2O$; then heating this at 130°, when it loses ethylenediamine and water, and finally extracting with water and crystallising. The salt is easily soluble in pyridine and in sulphuric acid, but is decomposed by heating with water. The chloride, $[Cr(C_2H_8N_2)_2(SCN)_2]Cl,H_2O$, is obtained in orange-yellow needles by treating the thiocyanate with concentrated hydrochloric acid. By treatment with hydrobromic acid, nitric acid, and sulphuric acid, the *bromide*, with $\frac{1}{2}H_2O$, the *nitrate*, with $1H_2O$, and the *hydrogen sulphate*, with $1\frac{1}{2}H_2O$, have been obtained, besides an acid chloride the composition of which appears to be variable.

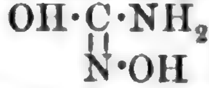
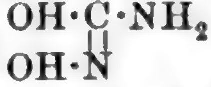
Ethylenediaminerhodosochromium salts. In the preparation of the luteochloride some rhodoso salt is also formed and is most easily isolated as ethylenediaminerhodosochromium bromide,

$$[Cr_2(C_2H_8N_2)_3O{\cdot}OH(H_2O)_2]Br_3,$$

which is obtained in transparent, red crystals. It is soluble in water and with potassium thiocyanate gives the thiocyanate.

The molecular weights of the luteoethylenediaminechromium salts, and the thiocyano-compounds described were determined by the cryoscopic method. J. McC.

Formation of Carbamide from Nitrogenous Substances. By Johann Plot (*Chem. Centr.*, 1901, ii, 1335—1336; from *Oesterr. Chem. Zeit.*, **4**, 485—487. Compare Jolles, Abstr., 1900, ii, 636; 1901, i, 30, 262, 583; this vol., i, 86).—In opposition to Jolles, the author considers that in the oxidation of purine compounds it is not the group $CO \cdot NH_2$ existing in these compounds which yields carbamide, but rather that the formation of carbamide results from the union of the decomposition products, ammonia and carbon dioxide, in presence of nascent carbonic acid (H_2CO_3). E. W. W.

Isomerism in the Hydroxyureas. By LUIGI FRANCESCONI and A. PARROZZANI (*Gazzetta*, 1901, **31**, ii, 334—347).—The action of hydroxylamine on potassium cyanate yields, in addition to the hydroxycarbamide described by Dresler and Stein (*Annalen*, 1869, **150**, 242), an isomeric compound to which the authors give the name *iso*hydroxycarbamide and the constitution  $\begin{array}{l}OH \cdot C \cdot NH_2 \\ \quad \| \\ \quad N \cdot OH\end{array}$. This compound and hydroxycarbamide (which is probably first produced in its tautomeric form having the structure  $\begin{array}{l}OH \cdot C \cdot NH_2 \\ \qquad \| \\ OH \cdot N\end{array}$ and then passes into the compound having the ordinary formula, $NH_2 \cdot CO \cdot NH \cdot OH$), are supposed to owe their formation to the fact that cyanic acid takes part in the reaction with hydroxylamine in its two tautomeric forms. This explanation is borne out by the observation that in the condensation of cyanic acid or of esters of *iso*cyanic acid with phenylhydroxylamine, no stereoisomerides are obtained, whilst in the action of esters of *iso*cyanic acid on hydroxylamine, derivatives of *iso*hydroxycarbamide seem to be produced although they have not as yet been isolated.

iso*Hydroxycarbamide*, $CH_4O_2N_2$, crystallises from ether in iridescent plates melting at 70—72° and completely decomposing into water, carbon dioxide, ammonia, and nitrogen, and is readily soluble in water, from which it is deposited unaltered; it is readily soluble in alcohol, moderately so in ether, and reduces Fehling's solution in the cold. With ferric chloride, it gives a transitory red coloration quite different from the blue colour obtained with hydroxycarbamide, into which it is transformed on heating in alcoholic solution. By boiling water, it is decomposed, with evolution of ammonia, into hydroxycarbamide and a substance giving a cherry-red coloration with ferric chloride. It has the normal molecular weight in freezing aqueous solution. Its *hydrochloride* separates in large, rectangular prisms which reduce Fehling's solution in the cold, and give a transitory rose-red coloration with ferric chloride; it is stable in a vacuum at the ordinary temperature. The *diacetyl* derivative, $C_5H_8O_4N_2$, crystallises from ether in mammillary masses, which melt at 105—106°, dissolve readily in alcohol, and give no reaction either with ferric chloride or with Fehling's solution; it has the normal molecular weight in freezing water, and when its aqueous solution is evaporated to dryness in a vacuum, a viscous residue remains which colours ferric chloride an intense red.

Potassium oxyfulminate, CO_2NK, obtained by the action of potassium hydroxide on *iso*hydroxycarbamide in absolute alcoholic solution, crystallises in needles which, with ferric chloride, give an intense blood-red coloration quickly changing to yellow; it reduces Fehling's solution on heating, and its aqueous solution evolves carbon dioxide on addition of hydrochloric acid; with silver nitrate, it gives a white, and with mercuric chloride a yellow, precipitate, both of which rapidly blacken. The electrical conductivity was determined, μ varying from 141·7 for a dilution $V=32$ to 159·9 for $V=1024$.

Methylhydroxycarbamide, $OH\cdot NH\cdot CO\cdot NHMe$, prepared from methylcarbimide and hydroxylamine, crystallises from ethyl acetate in rhomboidal plates melting and decomposing at 127° and is very soluble in water, less so in methyl and ethyl alcohols, and slightly in ether; it gives the characteristic bluish-violet coloration with ferric chloride and reduces Fehling's solution. No other compound could be isolated from the products of the reaction yielding methylhydroxycarbamide, but after the separation of the latter a viscous substance remained which, with ferric chloride, gave a rose-red coloration.

Ethylhydroxycarbamide, $OH\cdot NH\cdot CO\cdot NHEt$, melts and decomposes at 129°, and is soluble in water and in methyl or ethyl alcohol.

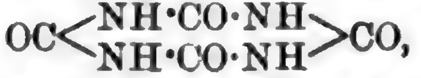
Phenylhydroxycarbamide, $OH\cdot NPh\cdot CO\cdot NH_2$, prepared by the action of hydrochloric acid on a mixture of phenylhydroxylamine and potassium cyanate, melts at 95°, is soluble in nearly all solvents, and gives with ferric chloride a dark bluish-violet coloration. Its *hydrochloride* is a white, crystalline, very deliquescent compound melting and decomposing at 90°.

Phenylmethylhydroxycarbamide, $OH\cdot NHPh\cdot CO\cdot NHMe$, prepared from methyl carbimide and phenylhydroxylamine, crystallises from benzene in mammillary aggregates of needles melting at 121°. Its *hydrochloride* separates in unstable acicular crystals which lose hydrogen chloride at 100°.

Phenylethylhydroxycarbamide, $OH\cdot NHPh\cdot CO\cdot NHEt$, crystallises from a mixture of benzene and ether in mammillary groups of needles melting at 93°. Its hydrochloride is unstable, and crystallises with difficulty.

The authors give details of improvements on Erdmann's method for preparing potassium cyanate (Abstr., 1894, i, 2). T. H. P.

New Oxidation Product of Uric Acid. By MAX SCHOLTZ (*Ber.*, 1901, **34**, 4130—4132).—*Tetracarbimide*,



$OC\left<\begin{matrix}NH\cdot CO\cdot NH\\NH\cdot CO\cdot NH\end{matrix}\right>CO$, is produced by oxidising sodium urate, dissolved in water, with a 3 per cent. solution of hydrogen peroxide, the reaction being accelerated by gently warming; the yield of this compound is only about 10 per cent. of the uric acid taken. The new product has no definite melting point but when heated evolves a pungent vapour which reddens lacmoid paper; it is insoluble in cold water and the ordinary organic solvents, but dissolves in hot water and sodium hydroxide solution. The *sodium* salt, $C_4H_3O_4N_4Na$, is very soluble in water but insoluble in alcohol. The *barium* salt, $C_4Ba_2O_4N_4$, is obtained as a crystalline precipitate by mixing hot solutions of tetracarbimide and barium hydroxide. The *calcium*, *silver*, *lead*, and *copper* salts are insoluble, the first two being amorphous whilst the others are crystalline.

G. T. M.

Chloroimides. By JOSEPH TSCHERNIAC [with A. BRAUN] (*Ber.*, 1901, **34**, 4209—4214).—The chloroimides of phthalic and succinic acids, when boiled with water, yield the imides and the acids together with nitrogen and chlorine, but no hypochlorous acid; neither is hypochlorous acid formed by the action of cold water on the chloroimides. The oxidising and bleaching properties of an aqueous solution of succinochloroimide are therefore due to the chlorine liberated. R. H. P

Adiponitrile. By LOUIS HENRY (*Bull. Acad. Roy. Belg.*, 1901, **7**, 367—372. Compare Abstr., 1886, 786, 860).—*Adiponitrile* (*aa'-dicyanobutane*), $C_4H_8(CN)_2$, obtained by the action of potassium cyanide on tetramethylene dibromide or di-iodide, is a thick, colourless, odourless liquid having a bitter taste; it boils at 295° under 760 mm. pressure, has a sp. gr. 0·951 at 19°/19°, and n_D 1·4397; the molecular refraction is 29·85, the calculated value being 29·70. When strongly cooled, it solidifies to a mass of long, needle-shaped crystals which melt at 0° to 1°. It readily combines with hydrogen bromide to form a white, crystalline mass, and on hydrolysis yields adipic acid. A review of the melting points of the dinitriles of the acids of the succinic series shows that those nitriles with an uneven number of carbon atoms melt at a lower temperature than those with an even number.

H. R. LE S.

Hydrazide and Azide [Azoimide] of Propionic and *iso*-Valeric Acids. By HERMANN HILLE (*J. pr. Chem.*, 1901, [ii], **64**, 401—418).—*Propionylhydrazide*, $CH_2Me\cdot CO\cdot N_2H_3$, prepared by boiling hydrazine hydrate with ethyl propionate and fractionating the product under reduced pressure, is an extremely hygroscopic solid melting at 40° and boiling at 130° under 16 mm. pressure; it reduces an ammoniacal solution of silver, and Fehling's solution; the *hydrochloride* forms a white, crystalline solid, melting and decomposing at 150°. *Propionylbenzylidenehydrazide*, $CH_2Me\cdot CO\cdot N_2H:CHPh$, prepared by the action of benzaldehyde on the hydrazide, crystallises in plates melting at 115°. *Propionyl-o-hydroxybenzylidenehydrazide*, $CH_2Me\cdot CO\cdot N_2H:CH\cdot C_6H_4\cdot OH$, crystallises in prisms melting at 184°; *propionyl-β-propylidenehydrazide*, $CH_2Me\cdot CO\cdot N_2H:CMe_2$, forms prisms melting at 101°. s-*Dipropionylhydrazide*, $N_2H_2(CO\cdot CH_2Me)_2$, prepared by long boiling of propionic anhydride and hydrazine hydrate, or by heating propionylhydrazide and propionic anhydride under pressure at 120°, crystallises in plates melting at 136° and boiling at 215—217° under 25 mm. pressure.

Propionylazoimide (propionylazide), $CH_2Me\cdot CO\cdot N_3$, prepared from propionylhydrazide hydrochloride and sodium nitrite, is an oil of disagreeable and irritating odour, readily volatile in ether vapour; with absolute alcohol, it yields ethylurethane; and with 50 per cent. alcohol, diethylcarbamide (m. p. 108°); from the latter, by heating with concentrated hydrochloric acid, ethylamine hydrochloride is obtained (m. p. 109°).

iso*Valerylhydrazide*, $CHMe_2\cdot CH_2\cdot CO\cdot N_2H_3$, prepared from ethyl *iso*valerate and hydrazine hydrate, crystallises in hygroscopic scales or needles melting at 68° and boils at 133° under 15 mm. pressure; the *hydrochloride* is crystalline, and melts and decomposes at 174°; iso*valerylbenzylidenehydrazide* $CHMe_2\cdot CH_2\cdot CO\cdot N_2H:CHPh$, crystallises in small plates melting at 95°. iso*Valeryl-o-hydroxybenzylidenehydrazide* crystallises in needles melting at 112°. iso*Valeryl-β-propylidenehydrazide*,

$CHMe_2{\cdot}CH_2{\cdot}CO{\cdot}N_2H{:}CMe_2$, crystallises in small plates melting at 67°.

s-*Divalerylhydrazide*, $N_2H_2(CO{\cdot}CH_2{\cdot}CHMe_2)_2$, is prepared by treating the monohydrazide in alcoholic solution with iodine and crystallises in long, prismatic plates melting at 182°.

iso*Valerylazoimide*, $CHMe_2{\cdot}CH_2{\cdot}CO{\cdot}N_3$, prepared by the action of sodium nitrite on valerylhydrazide hydrochloride, is an unstable, colourless solid which, on boiling with absolute alcohol, yields *iso*butylurethane (b. p. 99° under 19 mm. pressure), and with 50 per cent. alcohol, *s*-di*iso*butylcarbamide (m. p. 128°). K. J. P. O.

Hydrazide and Azide [Azoimide] of Palmitic Acid. By F. H. Dellschaft (*J. pr. Chem.*, 1901, [ii], **64**, 419—438).—*Palmitylhydrazide*, $C_{15}H_{31}CO{\cdot}N_2H_3$, prepared by adding ethyl palmitate to hydrazine hydrate, crystallises in needles melting at 111°; the *hydrochloride* forms small needles melting at 138—143°. *Palmitylbenzylidenehydrazide*, $C_{15}H_{31}{\cdot}CO{\cdot}N_2H{:}CHPh$, prepared from the hydrazide and benzaldehyde, crystallises in microscopic needles melting at 78°. *Palmityl* o-*hydroxybenzylidenehydrazide* is a crystalline solid melting at 104°, and the compound with ethyl acetoacetate,

$$C_{15}H_{31}{\cdot}CO{\cdot}N_2H{:}CMe{\cdot}CH_2{\cdot}CO_2Et,$$

prepared from the hydrazide and ethyl acetoacetate, crystallises in small, white needles, which become soft and yellow at 79° and finally melt at 122°. *Palmityl-β-propylidenehydrazide*, $C_{15}H_{31}{\cdot}CO{\cdot}N_2H{:}CMe_2$, prepared from the hydrazide and acetone, forms microscopic, crystalline needles which melt at 71°. *Acetylpalmitylhydrazide*,

$$C_{15}H_{31}{\cdot}CO{\cdot}N_2H_2Ac,$$

prepared by boiling the hydrazide with acetic anhydride, crystallises in small needles melting at 129°. *Benzoylpalmitylhydrazide*,

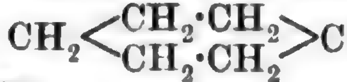
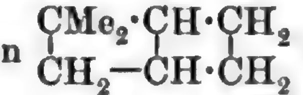
$$C_{15}H_{31}{\cdot}CO{\cdot}N_2H_2Br,$$

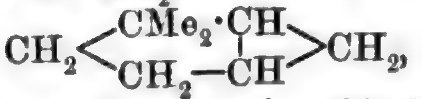
prepared by warming the hydrazide with benzoyl chloride, crystallises in microscopic needles which soften at 100° and melt at 108°. *Palmitylhydrindylhydrazide*, $C_{15}H_{31}{\cdot}CO{\cdot}N_2H{:}CH{\cdot}C_9H_9$, prepared from hydrindaldehyde and the hydrazide, crystallises in white needles melting at 86°.

s-*Dipalmitylhydrazide*, $N_2H_2(CO{\cdot}C_{15}H_{31})_2$, prepared by the action of iodine on an alcoholic solution of the hydrazide, crystallises in small, insoluble needles melting at 147°.

Palmitylazoimide, $C_{15}H_{31}{\cdot}CO{\cdot}N_3$, prepared by the action of nitrous acid (nitrous fumes) on the hydrazide hydrochloride, forms crystals melting at 49° and decomposing at 60°. With absolute alcohol, pentadecylethylurethane (m. p. 51°) is formed; with boiling water, *s*-dipentadecylcarbamide (m. p. 110°); with aniline, palmitylanilide (m. p. 87·5°), and with ammonia, palmitylamide. Pentadecylamine is obtained when the urethane is boiled with concentrated hydrochloric acid; the amine yields insoluble compounds with mercuric and cadmium chlorides. K. J. P. O.

Mixed Organo-magnesium Compounds and their Application to the Synthesis of Acids, Alcohols, and Hydrocarbons. By Victor Grignard (*Ann. Chim. Phys.*, 1901, **24**, [vii], 433—490).—A *résumé* of work already published (compare Abstr., 1900, i, 382; 1901, i, 250, 316, 393, 679). G. T. M.

Dimethylhexamethylene from Camphoric Acid. By Nicolai D. Zelinsky and N. Lepeschkin (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 549—565).—It has been previously shown (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 407) by the authors that from *iso*laurolene a hydrocarbon, C_8H_{16}, can be obtained which, from its physical properties, must be a hexamethylene derivative. This compound, to which the name dihydro*iso*laurolene is given, the authors have now prepared by the following four methods: (1) By the action of concentrated hydriodic acid on *iso*laurolene at 200°. (2) By the reduction of the liquid *iso*laurolene hydriodide (see below) by means of hydrogen in presence of a zinc-palladium couple (see Abstr., 1899, i, 181). (3) By the action of concentrated sulphuric acid on *iso*laurolene. (4) By the reduction of laurolene hydriodide by means of hydrogen in presence of a zinc-palladium couple. As obtained by these different methods, dihydro*iso*laurolene has slightly varying properties, due probably to small quantities of impurities difficult to remove. The product yielded by method (1) is a pleasant smelling liquid boiling at 114° (corr.) and having the sp. gr. 0·7686 at 17°/4°, n_D 1·4223 at 17°, and the molecular refraction (Lorentz and Lorenz' formula) 37·05, the number calculated from the structural formula given below being 36·82. The authors conclude that dihydro*iso*laurolene is a dimethylhexamethylene, and as the *o*-, *m*-, and *p*-dimethylhexamethylenes have been already prepared and characterised, it must be 1 : 1-dimethylhexamethylene,  $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CMe_2$. To *iso*laurolene the constitution  $\begin{matrix}CMe_2\cdot CH\cdot CH_2\\ | \qquad | \qquad | \\ CH_2-CH\cdot CH_2\end{matrix}$ is given and to laurolene,



$$CH_2<\begin{matrix}CMe_2\cdot CH\\ \qquad | \\ CH_2-CH\end{matrix}>CH_2,$$

which would explain the ready conversion of its hydriodide into dimethylhexamethylene by reduction; the fact that the carbon-atom rings in laurolene and in its hydriodide are identical is shown by the action of dimethylaniline on the latter compound, by which means laurolene is reformed. It is probable that camphoric acid, which readily gives up carbon dioxide with the formation of laurolene, also contains a six carbon atom ring.

When *iso*laurolene or its hydrobromide is heated with concentrated hydrobromic acid in a sealed tube, a colourless, liquid, isomeric *hydrobromide* is obtained which boils at 70—71° under 15 mm. pressure, and slowly decomposes on keeping. The liquid *hydriodide* obtained in a similar manner is faintly coloured, and boils at 75—80° under 15—17 mm. pressure. On heating *iso*laurolene hydriodide with diethylaniline, *iso*laurolene is obtained.

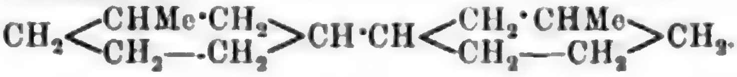
The action of concentrated sulphuric acid on *iso*laurolene yields dihydro*iso*laurolene and a mobile *liquid* having the empirical composition C_8H_{13}, and boiling at 259—260° under the ordinary pressure.

The laurolene obtained by the distillation of camphoric acid is probably not an individual compound but a mixture of isomerides. Laurolene as thus prepared was found to diminish in specific rotation ($[\alpha]_D$)

from 22·9° to 16·2° on treatment with permanganate, whilst the sp. gr. and refractive index also show slight changes. T. H. P.

Heats of Combustion of Cyclic Compounds. I. By P. Zuboff (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 708—722).—By means of a calorimetric bomb, the author has measured the heats of combustion of a large number of cyclic compounds prepared by Zelinsky; the results, expressed in calories per gram-molecule on the basis of Regnault's determination of the specific heat of water at 20°, are as follows:

Hydrocarbons.

		Constant volume.	Constant pressure.
C_6H_{14}.	Normal hexane	997·8	999·8
C_6H_{12}.	Methyl*cyclo*pentane	945·7	947·4
	*cyclo*Hexane	943·4	945·1
C_7H_{14}.	1 : 3-Dimethyl*cyclo*pentane	1099·5	1101·5
	Methyl*cyclo*hexane	1100·8	1102·8
	*cyclo*Heptane	1096·3	1098·3
C_8H_{16}.	1 : 1-Dimethyl*cyclo*hexane	1252·8	1255·1
	1 : 3-Dimethyl*cyclo*hexane	1248·1	1250·4
	1 : 4-Dimethyl*cyclo*hexane	1238·9	1241·2
C_9H_{18}.	1 : 3 : 3-Trimethyl*cyclo*hexane	1406·0	1408·6
C_7H_{12}.	Methyl*cyclo*hexene (α)	1047·6	1049·3
	Methyl*cyclo*hexene (β)	1053·2	1054·9
	*cyclo*Heptene	1058·7	1060·5
C_8H_{14}.	Laurolene	1202·8	1204·8
	*iso*Laurolene	1203·4	1205·3
$C_{14}H_{26}$.	 $CH_2{<}{}^{CHMe\cdot CH_2}_{CH_2-CH_2}{>}CH\cdot CH{<}{}^{CH_2\cdot CHMe}_{CH_2-CH_2}{>}CH_2$.	2123·5	2127·3

Alcohols.

$C_6H_{12}O$.	β-Methyl*cyclo*pentanol	895·1	896·6
	*cyclo*Hexanol	897·3	898·8
$C_7H_{14}O$.	1 : 3-Dimethyl*cyclo*pentanol (2)	1039·2	1040·9
	β-Methyl*cyclo*hexanol	1047·2	1048·9
	*cyclo*Heptanol	1059·0	1060·7
$C_8H_{16}O$.	1 : 3-Dimethyl*cyclo*hexanol (2)	1206·0	1208·0
	1 : 3-Dimethyl*cyclo*hexanol (5)	1193·1	1195·1
$C_9H_{18}O$.	$C_7H_{13}\cdot CHMe\cdot OH$	1353·4	1355·7

Ketones.

C_5H_8O.	Acetyltrimethylene	697·5	698·4
$C_6H_{10}O$.	β-Methyl*cyclo*pentanone	840·7	841·9
$C_7H_{12}O$.	β-Methyl*cyclo*hexanone	1003·4	1004·9
	*cyclo*Heptanone	1005·1	1006·6
$C_8H_{14}O$.	1 : 3-Dimethyl*cyclo*hexanone (2)	1139·5	1141·2
$C_9H_{16}O$.	1 : 4-Methylacetyl*cyclo*hexane	1278·8	1280·8
	$C_6H_{11}\cdot COEt$	1300·7	1302·7
	$C_7H_{13}\cdot COMe$	1289·4	1291·4
$C_8H_{12}O$.	1 : 3-Dimethyl*cyclo*-6-hexene-5-one	1111·8	1113·3
$C_9H_{14}O$.	1 : 1 : 5-Trimethyl*cyclo*-5-hexene-3-one	1259·2	1260·9

Nitrogen compounds.

$C_5H_{11}N$.	1 : 1-Amino*cyclo*propylethane	830·2	831·5
$C_7H_{15}N$.	3-Amino-1-methyl*cyclo*hexane	1128·0	1129·9
$C_9H_{19}N$.	$C_7H_{13}\cdot CHMe\cdot NH_2$	1440·1	1442·6
$C_9H_{17}NO$.	$C_7H_{13}\cdot CMe{:}NOH$	1375·3	1377·2

In some cases where only small quantities of isomeric cyclic compounds were available, the numbers differ to some extent, but, for such isomerides, the author is of opinion that the heats of combustion are either equal or very nearly so. T. H. P.

Piperylene and Tropilidene. By JOHANNES THIELE (*Annalen*, 1901, **319**, 226—230).—Piperylene, when oxidised with potassium permanganate solution, yields formic and acetic acids, a result which indicates that its constitution is that of αγ-pentadiene, $CH_2:CH\cdot CH:CHMe$. If the hydrocarbon were divinylmethane, it should yield malonic acid. The hydrocarbon obtained by Armstrong and Miller (Trans., 1886, **49**, 74) from compressed oil gas is identical with piperylene. The piperylene tetrabromide (αβγδ-tetrabromopentane) employed in characterising the hydrocarbon may crystallise either in prisms or leaflets melting at 114—115°. Divinylmethane should be the first product of the decomposition of dimethylpiperidine; the shifting of the double linkings may be due to the action of the trimethylamine; a similar action is observed in the preparation of *cyclo*heptadiene, these examples illustrating the attraction of double linkings. Piperylene and tropilidene do not condense with benzophenone or ethyl oxalate in the presence of an alkali ethoxide, and the latter hydrocarbon does not react with diazobenzenesulphonic acid. This result is all the more surprising because tropilidene is undoudtedly a *cyclo*heptatriene. G. T. M.

Thiosulphates of Aromatic Amines. By A. WAHL (*Compt. rend.*, 1901, **133**, 1215—1217).—On mixing solutions of sodium thiosulphate and aniline hydrochloride, *aniline thiosulphate*, $(NPhH_2)_2,H_2S_2O_3$, is formed as a crystalline precipitate. Other primary amines of the benzene and naphthalene series yield similar thiosulphates; secondary and tertiary amines, on the other hand, do not give these salts, but react with the thiosulphate with formation of sulphur and sulphur dioxide. Such bases as dimethyl-*p*-phenylenediamine yield thiosulphates of the type $NMe_2\cdot C_6H_4\cdot NH_2,H_2S_2O_3$. When heated, these salts are decomposed, giving the base, sulphur dioxide, sulphur, and water.

Nitrosodimethylaniline hydrochloride and sodium thiosulphate, when warmed together in aqueous solution, yield dimethyl-*p*-phenylenediamine sulphonic acid, representing 12—15 per cent. of the nitrosodimethylaniline used. K. J. P. O.

Derivatives of *p*-Tolyl-α-naphthylamine. By ROBERT GNEHM and ED. A. RÜBEL (*J. pr. Chem.*, 1901, [ii], **64**, 497—517).—*Acetyl*-p-*tolyl-α-naphthylamine*, $C_{19}H_{17}ON$, crystallises from ethyl acetate in small, white or pale flesh-coloured crystals, melts at 124°, and dissolves readily in organic solvents; it is not hydrolysed by dilute sulphuric acid at 120—140°, or by dilute alcoholic potassium hydroxide, but is hydrolysed by a 20 per cent. solution. The *benzoyl* derivative, $C_{24}H_{19}ON$, separates from ethyl acetate in yellow crystals, melts at 140°, and is hydrolysed much more readily than the acetyl derivative. The acetyl derivative is best sulphonated by leaving it with five times its weight of sulphuric monohydrate during two weeks; by this method, a *monosulphonic* acid is produced of which the *barium* salt was analysed. *Barium* p-*tolyl-a-naphthylaminesulphonate* was prepared by hydrolysing the acetyl derivative with alcoholic potassium hydroxide, but was not obtained pure; the hydrolysis could not be carried out by boiling the diluted sulphonation mixture as in the case of acetyldiphenylaminesulphonic acid or by using hydrogen chloride or iodide.

p-*Tolyl-a-naphthylnitrosoamine*, $C_{17}H_{14}ON_2$, separates from alcohol or ether in golden-yellow crystals, and melts at 102°. Alcoholic hydrogen chloride converts it into the isomeric p-*tolyl-4-nitroso-a-naphthylamine* which crystallises from alcohol in blood-red needles and melts at 161°; the *hydrochloride* forms brownish-black flakes with a bronze-like lustre, and melts at 173°. The hydrochloride condenses with β-naphthol to form an oxazime-dye, and is reduced by zinc dust to a diamine. The nitroso-base condenses with *p*-nitrobenzoyl cyanide to form p-*tolylamino-a-naphthyl-4-cyanazomethine*-p-*nitrophenyl*,

$$C_6H_4Me\cdot NH\cdot C_{10}H_6\cdot N\vdots C(CN)\cdot C_6H_4\cdot NO_2,$$

which separates from benzene in violet flakes with a bronze-like lustre, and from alcohol in brown, bronzy flakes, melts at 218°, and is hydrolysed by dilute acids to a diamine and nitrobenzoyl cyanide.

Nitroacetyl-p-*tolyl-a-naphthylamine*, $C_{19}H_{16}O_3N_2$, prepared by the action of nitric acid on *p*-tolyl-a-naphthylamine dissolved in acetic acid, crystallises from acetic acid and ethyl acetate, melts at 240°, and is not volatile with steam. When hydrolysed with alcoholic potassium hydroxide, it gives a yellow *nitrotolylnaphthylamine*, $C_{17}H_{14}O_2N_2$, which melts at 114°; an isomeric *nitro*-derivative, melting at 188°, was obtained by direct nitration of *p*-tolylnaphthylamine. *Trinitro*-p-*tolylnaphthylamine*, $C_{17}H_{12}O_6N_4$, melts at 245°, is insoluble in most solvents but dissolves in nitrobenzene and in aqueous alkalis.

Monobromo-p-*tolyl-a-naphthylamine*, $C_{17}H_{14}NBr$, melts at 220°, and is insoluble in all the ordinary solvents.

Tetrabromo-p-*tolyl-a-naphthylamine*, $C_{17}H_{11}NBr_4$, separates from benzene in well-formed crystals, melts at 162°, and is only slightly soluble in alcohol. By using a larger quantity of bromine, an isomeric *tetrabromo*-derivative was obtained, which crystallises in tablets and melts at 212°, together with a *hexabromo*-derivative, $C_{17}H_9NBr_6$, which crystallises in short, greenish-yellow prisms, melts at 185°, and is slowly decomposed by heating at 115°.

p-Tolyl-a-naphthylamine condenses with nitrosodimethyl-*m*-aminophenol to a quinoneimine-dye; the *colour-base*, $C_{25}H_{21}ON_3$, forms minute, brownish-red needles, and melts at 199°; it can also be prepared from Meldola's blue and *p*-toluidine. The homologous *base*, $C_{27}H_{25}ON_3$, prepared by condensation with nitrosodiethyl-*m*-aminophenol, forms green needles, and melts at 209·5°.

A table is given showing the absorption spectra of this series of dyes.

T. M. L.

Pseudophenols. By KARL AUWERS (*Ber.*, 1901, **34**, 4256—4267).—A discussion of the results previously obtained (see Abstr., 1900, i, 96 and 161) and those detailed in the following three abstracts. The term pseudophenols is proposed for such as are insoluble in alkalis. With *o*- or *p*-cresol derivatives which contain one of the following substituents in the side chain—chlorine, bromine, iodine, $-NO_2$, or an acyl group—the compounds are insoluble in alkalis. When the substituent is $-OH$, $-OR$, $-CN$, $-CO_2H$, or a positive radicle, the compounds are true phenols. These results, however, are subject to variation when there are substituents in the nucleus. R. H. P.

Nitro- and Thiocyano-pseudophenols and Cyanophenols. By Karl Auwers, C. Schumann [and, in part, Broicher] (*Ber.*, 1901, **34**, 4267—4282. See preceding abstract).—The compound previously described (Abstr., 1896, i, 421) as dibromo-ψ-cumenol nitrite is a nitro-compound, and is best obtained by the action of silver nitrite on the acetate of dibromo-ψ-cumenol bromide. Its *acetyl* derivative crystallises in felted needles, melts at 155—156°, and when warmed with sodium methoxide yields dibromo-*p*-hydroxy-ψ-cumyl methyl ether. The free nitro-derivative of the pseudophenol is obtained in two forms by the action of sodium methoxide at the ordinary temperature on its acetate, namely, a stable melting at 135° (*loc. cit.*) and a labile one melting at 110°. Silver nitrate reacts with acetyldibromo-ψ-cumenol bromide, forming *dibromo-*p*-acetoxy-ψ-cumyl nitrate*, which crystallises from methyl alcohol in slender, yellowish-white needles, and melts at 137—138°. The bromide of the phenol does not react with silver nitrate in the same way, but yields either dibromo-*p*-hydroxy-ψ-cumyl alcohol or the corresponding *ether* which melts at 254—255°. Analogous results were obtained by the action of silver nitrite and nitrate on the acetate of dibromo-*p*-hydroxymesityl iodide; the *acetyl* derivative of the nitro-compound crystallises in slender needles melting at 141° and, when hydrolysed with a cold solution of sodium methoxide, yields the stable form of the *nitro*-compound which crystallises in needles melting at 127—128°; the *acetyl* derivative of the nitrate crystallises in slender needles melting at 153—154°.

*Dibromo-*p*-hydroxy-ψ-cumyl thiocyanate*,

$\mathrm{SCN{\cdot}CH_2{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{CH{:}CH}}{\mathrm{CH{\cdot}CH}}{>}\mathrm{C{\cdot}OH}$, obtained by the action of potassium thiocyanate on dibromo-ψ-cumenol bromide, crystallises from light petroleum in needles, melts at 112—113°, and is not dissolved by aqueous alkalis without decomposition; the *acetyl* derivative, which can only be obtained from the acetyl derivative of the bromide, crystallises in lustrous leaflets, melts at 145—146°, and when hydrolysed with aqueous alkalis, yields the sulphide, $S(CH_2\cdot C_6Me_2Br_2\cdot OH)_2$ (Abstr., 1897, i, 35). The *diacetyl* derivative of the sulphide crystallises in needles and melts at 232—233°. The *methyl* ether of the thiocyanate is obtained when the reaction between potassium thiocyanate and the bromide is carried out in absolute alcoholic solution; it crystallises in lustrous leaflets, melts at 107—108°, and when treated with sodium methoxide yields the *dimethyl ether* of the disulphide, $S_2(CH_2\cdot C_6Me_2Br_2\cdot OMe)_2$, which crystallises in felted needles melting at 187—188°, and the *methyl ether* of the mercaptan, $OMe\cdot C_6Me_2Br_2\cdot CH_2\cdot SH$, which crystallises in needles melting at 94—95°.

When the acetyl derivative of dibromo-ψ-cumenol bromide is treated with potassium cyanide, a mixture of *dibromo-*p*-acetoxy-ψ-cumyl cyanide*, $OAc\cdot C_6Me_2Br_2\cdot CH_2\cdot CN$, and the *dibromo-*p*-acetoxy-ψ-cumyl ether* of dibromo-*p*-hydroxy-ψ-cumyl cyanide is obtained; the former is the more soluble in alcohol and crystallises in lustrous leaflets melting at 159—161°, the latter crystallises in slender, felted needles melting at 242—243°. *Dibromo-ψ-cumenol cyanide*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot CN$, crystallises in slender, white needles melting at 171°, is soluble in alkalis and sodium carbonate, and when hydrolysed yields *dibromo-*p*-hydroxy-*p*-xylylacetic acid*, which crystallises in slender, white needles and melts at 216—218°. R. H. P.

Pseudophenols. By O. STEPHANI (*Ber.*, 1901, **34**, 4283—4291. See preceding abstracts).—3 : 5-*Dibromo-2-hydroxybenzyl thiocyanate*,

$$OH\cdot C_6H_2Br_2\cdot CH_2\cdot SCN,$$

obtained when dibromosaligenin dibromide is treated with potassium thiocyanate, crystallises in colourless clusters of needles melting at 111—112°, is insoluble in alkalis, and forms an *acetyl* derivative, which crystallises in thick, yellowish needles melting at 148—150°. 2 : 3 : 6-*Tribromo-3-hydroxybenzyl thiocyanate* crystallises in thick, yellowish needles melting at 121—122°, and is soluble in cold alkalis; its acetyl derivative crystallises in silky needles, and melts at 115°. 3 : 5-*Dibromo-4-hydroxybenzyl thiocyanate* crystallises in lustrous laminæ melting at 108—109°, and is decomposed by alkalis.

The *acetyl* derivative of dibromosaligenin iodide crystallises from alcohol in needles, melts at 116—117°, and when treated with silver nitrite yields 3 : 5-*dibromo-2-acetoxyphenylnitromethane*,

$$OAc\cdot C_6H_2Br_2\cdot CH_2\cdot NO_2,$$

which crystallises in lustrous, slender needles, and melts at 132—133°; the corresponding *hydroxy*-compound crystallises in yellowish needles melting at 92—93°, and is decomposed by cold alkalis.

2 : 3 : 6-*Tribromo-3-acetoxybenzyl iodide* crystallises in yellowish needles melting at 119—120°. *Tribromo-3-hydroxyphenylnitromethane* crystallises in thick needles melting at 135—136°, and is soluble in alkalis.

In the course of this and previous researches of Auwers (*loc. cit.*), it was shown that of the dibromo-ψ-cumenol haloids the chloride is the least stable, and the author's attempt to prepare the fluoride failed.

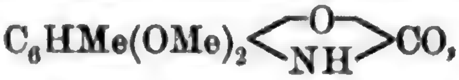
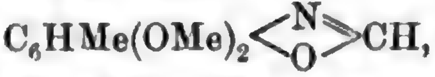
*Ethyl dibromo-*p*-hydroxy-ψ-cumylmalonate*,

$$OH\cdot C_6Br_2Me_2\cdot CH_2\cdot CH(CO_2Et)_2,$$

obtained by the action of the ψ-cumyl chloride on ethyl malonate in the presence of sodium, crystallises in plates melting at 92—93°; the *acid*, when heated at 173°, yields *dibromo-*p*-hydroxycumylacetic acid*, which crystallises in yellowish needles, melts at 170—171°, and is not altered when boiled with alkalis.

The *formate* and *amyl ether* of dibromo-*p*-hydroxy-ψ-cumyl alcohol were found to be similar in properties to analogous compounds previously described (*loc. cit.*); the formate crystallises in slender, white needles melting at 150—152°, and the amyl ether forms rhombic crystals melting at 84·5°. R. H. P.

Nitroso-derivative of Methylphloroglucinol Dimethyl Ether. By JACQUES POLLAK and M. SOLOMONICA (*Monatsh.*, 1901, **22**, 1002—1010).—The constitution of the monomethyl ether of methylphloroglucinol having been shown by Konya (Abstr., 1900, i, 545) to be [OH : OH : Me : OMe = 1 : 3 : 2 : 5], that of the dimethyl ether must be [OH : OMe : Me : OMe = 1 : 3 : 2 : 5].

The nitroso-derivative melts at 160°, and is reduced by stannous chloride to the corresponding amino-hydrochloride, which yields a triacetyl derivative melting at 152—155°. When heated with carbamide, the hydrochloride of the base is converted into 3 : 5-*dimethoxy-2-methylcarbonyl-6-aminophenol*,  $C_6HMe(OMe)_2{<}\substack{O\\NH}{>}CO$, which crystallises from alcohol in delicate, greyish-white needles melting at 188—189°. On oxidation with ferric chloride, the base yields 3-*hydroxy-5-methoxy-2-methylquinone*; this crystallises in delicate red needles which melt at 183—185°. Etherification of the nitroso-derivative by sodium methoxide and methyl iodide leads to the formation of the methenyl compound,  $C_6HMe(OMe)_2{<}\substack{N\\O}{>}CH$, which crystallises in yellow leaves melting at 72—74°. These reactions show the *nitrosomethylphloroglucinol dimethyl ether* to have the nitroso-group in the *ortho*-position relatively to the hydroxyl. G. Y.

Chloromethyl Benzoate and Methylene Dibenzoate. By MARCEL DESCUDÉ (*Compt. rend.*, 1901, **133**, 1213—1214. Compare Abstr., 1901, i, 504, 644).—*Chloromethyl benzoate* (*loc. cit.*) is a colourless liquid which boils at 210° under 740 mm. pressure and at 120—122° under 12 mm. pressure, and has a sp. gr. 1·236 at 20°. Methylene dibenzoate is formed when chloromethyl benzoate is heated with dried potassium benzoate at 150°; gaseous ammonia and the dibenzoate yield primarily benzamide and formaldehyde, which react together forming methylenedibenzamide (m. p. 218°); at the same time, ammonium benzoate and hexamethylenetetramine are produced.

K. J. P. O.

2-Chloro-3-naphthoic Acid. By ERICH STROHBACH (*Ber.*, 1901, **34**, 4158—4162).—2-*Chloro-3-naphthoyl chloride*, $C_{10}H_6Cl{\cdot}COCl$, prepared by heating 2-hydroxy-3-naphthoic acid and phosphorus pentachloride (3 mols.) at 200—210°, is an almost colourless, highly refractive oil boiling at 248° under 160 mm. pressure, which solidifies at 56·5° to a mass of lustrous needles. The acid chloride when warmed with water yields 2-chloro-3-naphthoic acid, this substance being obtained in snow-white crystals melting at 216·5° (compare Hosaeus, Abstr., 1893, i, 355).

Ethyl 2-chloro-3-naphthoate, $C_{10}H_6Cl{\cdot}CO_2Et$, produced by ethylating the acid with absolute alcohol and hydrogen chloride, crystallises from methyl alcohol in white leaflets; it melts at 50° and boils at 218—222° under 160 mm. pressure.

2-*Chloro-3-naphthamide*, $C_{10}H_6Cl{\cdot}CO{\cdot}NH_2$, formed by adding 2-chloro-3-naphthoyl chloride to concentrated ammonia solution, crystallises from glacial acetic acid in white needles melting at 236—237°.

1-*Chloro-2-naphthoyl chloride*, $C_{10}H_6Cl{\cdot}COCl$, prepared from 1-hydroxy-2-naphthoic acid and phosphorus pentachloride, crystallises from ether in aggregates of needles and melts indefinitely between 48° and 60·5°; after solidifying, it melts at 64—65°. When distilled under 160 mm. pressure, the chloride boils at 226°; it seems to contain traces of 1-chloro-2-naphthoyl trichloride. G. T. M.

Chlorobromo-3-hydroxybenzoic Acids and their Ethyl Esters. By C. MARTINI (*Gazzetta*, 1901, **31**, ii, 363—370).—*Ethyl* 6-*chloro*-2-*bromo*-3-*hydroxybenzoate*, $OH\cdot C_6H_2ClBr\cdot CO_2Et$, obtained by the action of bromine on ethyl 6-chloro-3-hydroxybenzoate in acetic acid solution, crystallises from aqueous alcohol in slender, white, anhydrous needles melting at 101—102°. The corresponding *acid*, prepared either by hydrolysis of the ethyl ester or by the action of bromine on 6-chloro-3-hydroxybenzoic acid, separates from aqueous alcohol in small, white needles containing $1H_2O$ and melting at 194—195°; in aqueous solution, the acid gives a brownish-violet coloration with ferric chloride.

Ethyl 2-*chloro*-6-*bromo*-3-*hydroxybenzoate*, obtained by the action of bromine on ethyl 2-chloro-3-hydroxybenzoate, separates from its ethereal solution, on cooling in ice and salt, as a pasty mass which liquefies at the ordinary temperature (24°) and is only slightly volatile in a current of steam. The corresponding *acid*, prepared either by hydrolysing the ethyl ester or by brominating 2-chloro-3-hydroxybenzoic acid, separates from aqueous alcohol in small, dense crystals which contain $1H_2O$ and melt with incipient decomposition at 116—118°; with ferric chloride, it gives a violet coloration.

The two acids above described and the corresponding dichloro-acid $[CO_2H : Cl : Cl : OH = 1 : 2 : 6 : 3]$ all crystallise with $1H_2O$, and their ethyl esters crystallise in an anhydrous state, and are only hydrolysed with difficulty, even by concentrated potassium hydroxide solutions.

T. H. P.

Some Derivatives of β-Cresotic Acid [2-Hydroxy-*m*-toluic Acid]. By MAX FORTNER (*Monatsh.*, 1901, **22**, 939—954).—Nitration of 2-acetoxy-*m*-toluic acid and subsequent hydrolysis yields 5-*nitro*-2-*hydroxy*-m-*toluic acid*, which melts at 199°. Contrary to Einhorn's statement (Abstr., 1900, i, 439), esterification of the nitro-acid takes place with hydrochloric acid and alcohol. The position of the nitro-group was determined by reduction of the ester to the amino-compound, which melted at 106°, and conversion of this, by Sandmeyer's reaction, into Thiele and Eichwede's *ethyl* 5-*bromo*-2-*hydroxy*-m-*toluate* $[Br : Me : OH : CO_2Et = 5 : 3 : 2 : 1]$, which melts at 75° (Abstr., 1900, i, 501). Hydrolysis of the ester yielded the 5-*bromo-acid* melting at 236°. The position of the nitro-group is also shown by comparison of 5-amino-2-hydroxy-*m*-toluic acid with that of Nietzki and Ruppert. 5-*Nitro*-2-*acetoxy*-m-*toluic acid* separates from alcohol in yellowish crystals which melt at 142°.

5-*Nitro*-2-*hydroxy*-m-*toluoyl chloride*, prepared by the action of thionyl chloride, forms small, yellowish crystals which melt at 86—88° and have a characteristic aromatic odour. From the chloride were prepared the *amide*, which forms small, yellow crystals melting at 231°; the *anilide*, yellowish needles which melt at 208°; the *piperidide*, which separates from alcohol in small, yellowish, glistening needles melting at 125°; the *phenylhydrazide*,

$$N_2HPh[CO\cdot C_6H_2Me(OH)\cdot NO_2]_2,$$

which separates slowly from alcohol or glacial acetic acid as a crystalline powder melting at 255°. The amide, anilide, and piperidide give deep red colorations with ferric chloride. Attempts to brominate 5-nitro-2-hydroxy-*m*-toluic acid were unsuccessful.

The 5-bromo-acid may also be prepared almost quantitatively by bromination of 2-hydroxy-*m*-toluic acid in chloroform solution.

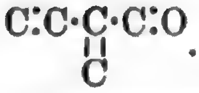
*5-Bromo-2-acetoxy-*m*-toluic acid* crystallises from alcohol in white needles which melt at 155°.

*5-Bromo-2-hydroxy-*m*-toluoyl chloride*, formed by the action of thionyl chloride, is easily soluble in benzene, from which it crystallises in rhombic plates melting at 80—85° and having a characteristic odour. From it were prepared the *ethyl ester*; the *amide*, which crystallises from alcohol in small leaves melting at 75—78°; the *anilide*, which melts at 125°; the *piperidide*, which melts at 82—84°. The amide, anilide, and piperidide give red to violet colorations with ferric chloride. G. Y.

Isomeric Dimethylcoumarones contained in Coal-tar. By JOHANNES BOES (*Chem. Centr.*, 1901, ii, 1226; from *Pharm. Zeit.*, **46**, 878).—Since the presence of *as-o*-xylenol and *as-p*-xylenol has been detected in the decomposition products of the coal-tar fraction boiling at 220—222° (Abstr., 1900, i, 31), this liquid, whilst consisting mainly of 4 : 6-dimethylcoumarone, must also contain a small quantity of 4 : 5-dimethylcoumarone, together, possibly, with traces of 3 : 6-dimethylcoumarone. E. W. W.

Organic Mercury Compounds. By JOHANNES BOES (*Chem. Centr.*, 1901, ii, 1347—1348; from *Pharm. Zeit.*, **46**, 915).—Coumarone and indene combine with mercuric sulphate to form the *compounds* $C_8H_6O,2HgSO_4,2HgO,H_2O$ and $C_9H_8,2HgSO_4,2HgO,H_2O$ respectively. These substances are best prepared by means of Denigès' mercuric sulphate solution (Abstr., 1895, i, 411) and are well suited for the quantitative separation of coumarone or indene from benzene solutions; they form yellow precipitates, are insoluble in water and the ordinary solvents, lose water at 100—110°, decompose above 200°, and when treated with hydrogen sulphide or warm hydrochloric acid regenerate the hydrocarbon.

The *compounds* $C_8H_6O,HgSO_4,2HgO$ and $C_9H_8,HgSO_4,2HgO$, prepared by shaking solutions of coumarone or indene respectively, diluted with pure methyl alcohol with the calculated quantity of a solution of mercuric sulphate, are also suitable, under certain conditions, for analytical purposes. E. W. W.

The Constitution of Unsaturated and Aromatic Compounds. By JOHANNES THIELE (*Annalen*, 1901, **319**, 129—143. Compare E. Erlenmeyer, jun., Abstr., 1901, i, 357, 373).—The formation of α-benzyl-β-benzylidenepropionic acid, $CHPh{:}CH{\cdot}CH(CH_2Ph){\cdot}CO_2H$, from αβ-dibenzylidenepropionic acid, $CHPh{:}CH{\cdot}C(CHPh){\cdot}CO_2H$, is no exception to the rule deduced from the author's theory that the hydrogen atoms should attach themselves to the ends of the system $C{:}C{\cdot}C{:}C$, for the unreduced compound also contains the conjugate system $C{:}C{\cdot}C{:}O$ interlaced with the other chain in the following manner,  $\mathrm{C{:}C{\cdot}\underset{\underset{C}{\|}}{C}{\cdot}C{:}O}$. The hydrogen atoms may therefore be considered to attach themselves to the ends of the system containing oxygen, forming the labile compound $\mathrm{CH_2Ph{\cdot}C(CH{:}CHPh){:}C(OH)_2}$, which is immediately transformed into the stable product

$$\mathrm{CH_2Ph{\cdot}CH(CH{:}CHPh){\cdot}CO_2H}.$$

This explanation applies equally well to the reduction of γ-phenyl-α-benzylidene-Δ^2-crotonolactone.

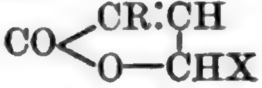
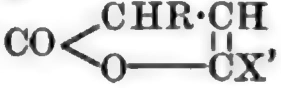
The existence of free triphenylmethyl has an important bearing on the theory of partial valency, and according to this hypothesis the fourth valency of the methyl carbon atom is almost entirely satisfied by the residual affinities of the carbon atoms of the aromatic nuclei.

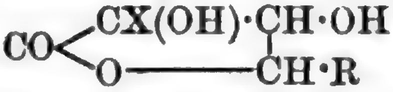
The space formula for benzene adopted by Erlenmeyer, jun., consists of six regular tetrahedra arranged so that their bases lie in the same plane, forming a hexagon, their apical angles being situated on the same side of this plane. The theoretical conclusions deduced from this formula as to the behaviour of aromatic compounds are, however, invariably opposed to the facts of experiment.

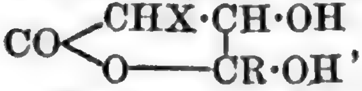
According to this hypothesis, the carboxyl groups in terephthalic, *iso*phthalic, and succinic acids have the same spacial relationship to each other, and the formation of anhydride should in each case take place with equal readiness. On this assumption, *p*-hydroxymethylbenzoic acid becomes an analogue of γ-hydroxybutyric acid and should readily furnish a lactone. These assumptions are directly opposed to the known behaviour of the compounds in question. Ethyleneglycol and catechol form monomolecular carbonates, but according to this hypothesis quinol is also an analogue of the glycol and should also accordingly yield a simple carbonate; resorcinol and quinol, however, both form polymeric carbonates.

The central carbon atoms of a naphthalene molecule produced by the conjugation of two such benzene nuclei would be united by a double linking, and this portion should accordingly be the one most susceptible to the attack of substituting agents. This conclusion is manifestly incorrect and a similar fallacy is detected on applying the same line of argument to the anthracene molecule. The employment of a modification of this space formula in which the apical angles of the tetrahedra are placed alternately on opposite sides of the plane of the nucleus is attended with similar disadvantages. G. T. M.

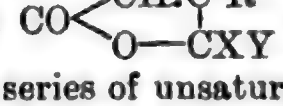
Unsaturated γ-Lactones. By JOHANNES THIELE (*Annalen*, 1901, **319**, 144—155. Compare following abstracts).—This theoretical communication contains a discussion of the four following memoirs.

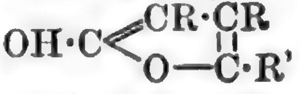
The saturated γ-ketonic acids give rise to two series of crotonolactones,  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CR{:}CH}\\ \mathrm{O{-}CHX}\end{array}$ and  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CHR{\cdot}CH}\\ \mathrm{O{-\!-}CX}\end{array}$ (with CH and CX doubly linked), these derivatives being indicated by the symbols Δ^{α} and Δ^{β} respectively. Sometimes a third isomeride is possible, as, for example, when the substituent X is a benzyl radicle; the isomerism of dihydrocornicularolactone and α-phenyl-γ-benzyl-Δ^{α}-crotonolactone is explained in this manner, these isomerides containing extra- and intra-nucleal double linkings respectively.

The Δ^{α}-lactones, on oxidation with permanganate, yield dihydroxylactones,  $\mathrm{CO}<\begin{matrix}\mathrm{CX(OH)\cdot CH\cdot OH}\\ \mathrm{O{-}{-}{-}{-}{-}CH\cdot R}\end{matrix}$, which in turn give rise to trihydroxyacids, $\mathrm{OH\cdot CHR\cdot CH(OH)\cdot CX(OH)\cdot CO_2H}$; this reaction is not, however, perfectly general, for $\beta\gamma$-diphenyl-Δ^{α}-crotonolactone is very slightly affected by the oxidising agent.

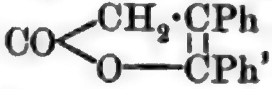
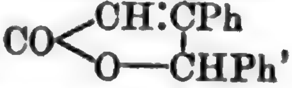
The Δ^{β}-lactones, on oxidation, yield hydroxyketonic acids, $\mathrm{R\cdot CO\cdot CH(OH)\cdot CHX\cdot CO_2H}$, the intermediate dihydroxylactones,  $\mathrm{CO}<\begin{matrix}\mathrm{CHX\cdot CH\cdot OH}\\ \mathrm{O{-}{-}{-}CR\cdot OH}\end{matrix}$, being unstable.

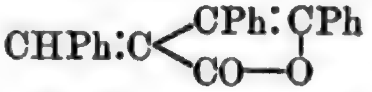
The lactones of this series containing in the α-position a methylene group between a carbonyl and an ethylene linking, readily condense with aldehydes in the presence of a weak base such as aniline; the corresponding Δ^{α}-derivatives do not react under these conditions. The Δ^{β}-derivatives are usually labile and are converted into their stable Δ^{α}-isomerides by the action of acetic anhydride or a strong base such as ammonia, tropine, piperidine, or the aliphatic amines. Bases with a neutral reaction (aniline, pyridine, or their derivatives) do not bring about this transformation. The Δ^{α}-compound, however, is not invariably the stable modification, for in the case of the γ-phenylcrotonolactones, the isomeride of this series is readily transformed into its Δ^{β}-isomeride. This characteristic action of the strong bases is analogous to that of alkaline reagents on the enolic forms of the esters of β-ketonic acids; in the latter case, a double linking shifts from the $\cdot\mathrm{C{:}C}\cdot$ to the $\mathrm{{:}C{:}O}$ group, whilst in the former, the rearrangement occurs between two $\cdot\mathrm{C{:}C}\cdot$ residues. The transformation of Δ^{β}-lactone into its Δ^{α}-isomeride is reversed when the strong base reacts in the presence of an agent capable of condensing with the regenerated Δ^{β}-lactone, the substance commonly employed being an aldehyde.

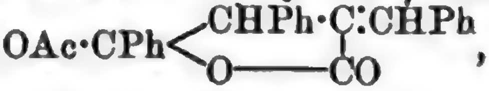
The reduction of ammoniacal silver nitrate by the Δ^{α}- and Δ^{β}-crotonolactones varies in rapidity with the position of the double linking, and it also seems to depend on the presence of hydrogen in the γ-position of the lactone ring, for derivatives having the general formula  $\mathrm{CO}<\begin{matrix}\mathrm{CH{:}C\cdot R}\\ \mathrm{O{-}CXY}\end{matrix}$ are not affected by this reagent.

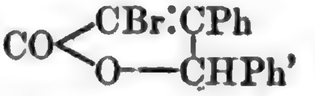
Both series of unsaturated lactones develop an intense yellow coloration with alcoholic potassium hydroxide, which is supposed to be due to the formation of hydroxyfurfuranols,  $\mathrm{OH\cdot C}<\begin{matrix}\mathrm{CR\cdot CR}\\ \mathrm{O{-}C\cdot R'}\end{matrix}$, substances which could be produced by a simple transformation from both Δ^{α}- and Δ^{β}-derivatives. Lactones such as phenylbenzylidenebutyrolactone and dihydrocornicularolactone, which contain a double linking outside the lactone ring, do not exhibit this property.

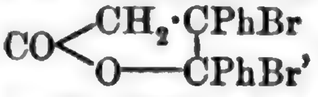
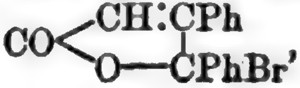
The following communications furnish experimental evidence in favour of the hypothesis that the two series of crotonolactones are structurally dissimilar and not stereoisomerides as suggested by Erlenmeyer, jun. (compare Abstr., 1901, i, 357, 373). G. T. M.

The Lactones of Desylacetic Acid. By JOHANNES THIELE and FRITZ STRAUS (*Annalen*, 1901, **319**, 155—180. Compare Abstr., 1899, i, 612; Klingemann, Abstr., 1892, 1002, and Erlenmeyer and Lux, Abstr., 1898, i, 668).—βγ-Diphenyl-Δ^{β}-crotonolactone,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH_2\cdot CPh}\\ \mathrm{O{—}CPh}\end{array}$, readily reduces ammoniacal silver nitrate and potassium permanganate solutions, and is converted into its stable Δ^{α}-isomeride,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH{:}CPh}\\ \mathrm{O{—}CHPh}\end{array}$, when boiled with alcohol containing traces of a base or salt having an alkaline reaction; the catalysts employed are potassium carbonate or hydroxide, sodium acetate, ammonia, piperidine, or an aliphatic amine. The aromatic bases do not promote this transformation.

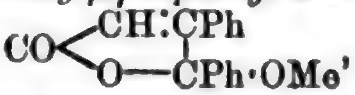
βγ-Diphenyl-α-benzylidene-Δ^{β}-crotonolactone,  $\mathrm{CHPh{:}C}<\begin{array}{l}\mathrm{CPh{:}CPh}\\ \mathrm{CO{—}O}\end{array}$, produced by boiling together its generators in alcohol containing a trace of aniline, crystallises from this solvent in yellow needles melting at 141—142°; it is also obtained by heating the stable lactone with benzaldehyde containing a few drops of piperidine. The latter mode of formation indicates that the transformation of the labile lactone with the Δ^{α}-isomeride by the aid of piperidine is a reversible process.

Desylcinnamic acid, $\mathrm{COPh\cdot CHPh\cdot C(CHPh)\cdot CO_2H}$, results from the action of a methyl alcoholic solution of potassium hydroxide on the preceding compound; it separates from benzene as a white, crystalline powder, and melts at 187—188°. The *methyl* ester, obtained from the silver salt and methyl iodide, crystallises from alcohol in lustrous, white needles and melts at 113·5°. The acid and its ester develop an intense yellow coloration with alcoholic potassium hydroxide, but it is destroyed by the addition of water. When treated with acetic anhydride and a trace of sulphuric acid, the acid yields *γ-acetoxy-βγ-diphenyl-α-benzylidenebutyrolactone*,  $\mathrm{OAc\cdot CPh}<\begin{array}{l}\mathrm{CHPh\cdot C{:}CHPh}\\ \mathrm{O{———}CO}\end{array}$, a substance crystallising from alcohol in colourless, iridescent plates melting at 128—128·5°.

α-Bromo-βγ-diphenyl-Δ^{α}-crotonolactone,  $\mathrm{CO}<\begin{array}{l}\mathrm{CBr{:}CPh}\\ \mathrm{O{—}CHPh}\end{array}$, prepared by treating thin layers of the powdered Δ^{α}-lactone with bromine vapour in the presence of light, crystallises from alcohol or carbon disulphide in colourless needles and melts at 118—119°; it is somewhat insoluble in the ordinary organic solvents, reduces ammoniacal silver nitrate, regenerates the Δ^{α}-lactone when treated with alcohol and a zinc-copper couple, but is not attacked by zinc dust and cold acetic acid.

βγ-Dibromo-βγ-diphenylbutyrolactone,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH_2\cdot CPhBr}\\ \mathrm{O{—}CPhBr}\end{array}$, produced by adding the Δ^{β}-lactone dissolved in carbon disulphide to a cooled solution of bromine in the same solvent, separates as a white, crystalline powder which decomposes at 64° evolving hydrogen bromide and yielding *γ-bromo-βγ-diphenyl-Δ^{α}-crotonolactone*,  $\mathrm{CO}<\begin{array}{l}\mathrm{CH{:}CPh}\\ \mathrm{O{—}CPhBr}\end{array}$, a substance crystallising from light petroleum in well-defined, brownish prisms, melting at 107—108° and decomposing at 130°.

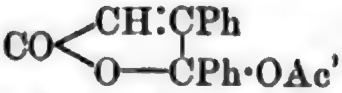
The mono-bromolactone yields the labile Δ^α-lactone on reduction with zinc dust and glacial acetic acid, and when warmed with methyl alcohol gives rise to *γ-methoxy-βγ-diphenyl-Δ^α-crotonolactone*,



$$\mathrm{CO}\Big<\begin{array}{l}\mathrm{CH{:}CPh}\\ \mathrm{O{-\!-}CPh{\cdot}OMe}\end{array},$$

which separates from this solvent in colourless crystals melting at 102·5°.

γ-Acetoxy-βγ-diphenyl-Δ^α-crotonolactone,



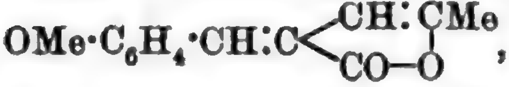
$\mathrm{CO}\Big<\begin{array}{l}\mathrm{CH{:}CPh}\\ \mathrm{O{-\!-}CPh{\cdot}OAc}\end{array}$, produced by shaking an ethereal solution of the bromo-lactone with silver acetate, crystallises from methyl alcohol or benzene, and melts at 116°.

Desyleneacetic acid, $\mathrm{COPh{\cdot}CPh{:}CH{\cdot}CO_2H}$, prepared from βγ-dibromo-βγ-diphenylbutyrolactone by the action of a cold alcoholic solution of potassium hydroxide, is also obtained by oxidising the Δ^β-lactone with a potassium permanganate solution containing magnesium sulphate, and is produced in small quantities along with desylacetic acid when the dibromide is converted into γ-bromo-βγ-diphenyl-Δ^α-crotonolactone by the action of heat; it crystallises from benzene and melts at 139°; the solidified product, however, has a melting point of 167°. The two modifications, when mixed together, melt at 167°. These two modifications of the acid seem to have a transformation temperature which is below the melting point of the substance melting at 139°; this form is distinguished as the α-, and the other as the β-compound. The α-acid, when heated at 130—135°, changes into the β-compound, whilst this substance, when dissolved in ammonia and precipitated by acid, regenerates the acid of lower melting point. The silver salts obtained from the two modifications yield the same *methyl* ester on treatment with methyl iodide; this derivative forms lustrous needles melting at 89°, and is isomeric with γ-methoxy-βγ-diphenyl-Δ^α-crotonolactone. Desyleneacetic acid may also be obtained from β-bromo-βγ-diphenyl-Δ^α-crotonolactone or γ-methoxy-βγ-diphenyl-Δ^α-crotonolactone by the action of alcoholic solutions of potassium hydroxide; it is identical with the product from desylenemalonic acid (Japp, Trans., 1895, 67, 138; 1897, 71, 133).

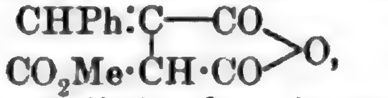
Ethyl desylenemalonate, $\mathrm{COPh{\cdot}CPh{:}C(CO_2Et)_2}$, when crystallised from alcohol, melts at 70—71°.

Deoxybenzoin is readily prepared by treating chlorobenzil with granulated zinc and alcoholic hydrochloric acid. G. T. M.

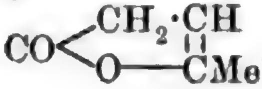
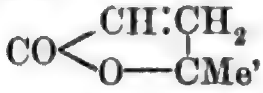
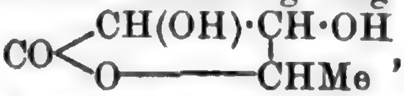
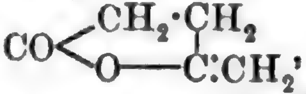
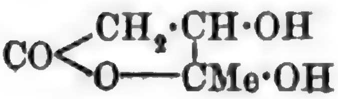
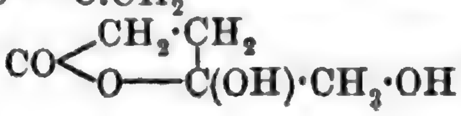
The Lactones of Angelic Acid. By JOHANNES THIELE, ROBERT TISCHBEIN and EMIL LOSSOW (*Annalen*, 1901, 319, 180—195).—$\Delta^\beta(\alpha)$-Angelicalactone, prepared from lævulic acid by Bredt's method (Abstr., 1890, 863), yields *α-anisylidene-Δ^β-angelicalactone*,



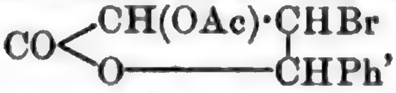
$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH{:}C}\Big<\begin{array}{l}\mathrm{CH{:}CMe}\\ \mathrm{CO{-\!-}O}\end{array}$, when condensed with anisaldehyde, and *α-benzylidenelævulic acid*, $\mathrm{COMe{\cdot}CH_2{\cdot}C(CHPh){\cdot}CO_2H}$; when treated with benzaldehyde; the former product crystallises from methyl alcohol in yellow needles melting at 98·5—99°, and the latter in white needles melting at 121° (compare Erdmann, Abstr., 1900, 375, 1129). The condensations are carried out in the presence of a trace of piperidine; when the reaction with benzaldehyde is performed in a methyl alcohol solution of potassium hydroxide, a *dibenzylidenelævulic acid* is obtained which forms colourless needles melting at 177—178°, and differs from Erdmann's βδ-dibenzylidenelævulic acid (*loc. cit.*)

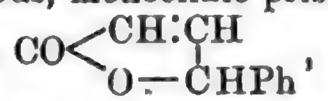
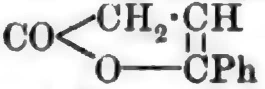
Benzylidenemalic acid, $HO\cdot CH(CO_2H)\cdot C(CHPh)\cdot CO_2H$, and iodoform are obtained on treating α-benzylidenelævulic acid with iodine and sodium hydroxide; the acid separates from water in white crusts melting at 173° and yields the *anhydride*,  $\begin{array}{l}\mathrm{CHPh{:}C{-}CO}\\ \mathrm{CO_2Me\cdot CH\cdot CO}\end{array}{>}\mathrm{O}$, of β-acetyl-α-benzylidenemalic acid, a substance crystallising from benzene and light petroleum in white needles melting at 116·5—117°. *α-Anisylidenelævulic acid*, $CH_2Ac\cdot C(CH\cdot C_6H_4\cdot OMe)\cdot CO_2H$, obtained from the corresponding lactone by treating it with crystallised sodium carbonate in dilute alcoholic solution and acidifying the product, crystallises from toluene in needles melting at 119—119·5°; the lactone is regenerated by the action of acetic anhydride and a trace of sulphuric acid.

Anisylidenemalic acid, $CO_2H\cdot CH(OH)\cdot C(CO_2H){:}CH\cdot C_6H_4\cdot OMe$, produced together with iodoform by the action of iodine and sodium hydroxide on the preceding acid, forms white needles sintering at 165° and decomposing at 177°.

The formation of condensation products from α-angelicalactone and the aldehydes shows that it has a constitution corresponding with the formula  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CH_2\cdot CH}\\ \mathrm{O{-}CMe}\end{array}$. It is partially transformed into the β- or Δ^{α}-angelicalactone,  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CH{:}CH_2}\\ \mathrm{O{-}CMe}\end{array}$, by heating with diethylaniline hydrobromide, or triethylamine; the converse transformation occurs to a limited extent on warming the purified Δ^{α}-isomeride with the latter reagent. Δ^{α}-Angelicalactone does not combine with anisaldehyde, but when oxidised with potassium permanganate solution containing magnesium sulphate yields *dihydroxyvalerolactone*,  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CH(OH)\cdot CH\cdot OH}\\ \mathrm{O{-}CHMe}\end{array}$, which crystallises from water, alcohol, or ethyl acetate in colourless needles melting at 100°; its *diacetyl* derivative, obtained by the action of acetyl chloride, crystallises from alcohol in colourless needles melting at 94—95°. Barium trihydroxyvalerate, produced by dissolving the lactone in barium hydroxide solution, is an uncrystallisable salt; the corresponding acid is unstable and regenerates the lactone. Alkaline solutions of the lactone do not reduce ammoniacal silver nitrate. The stability of the dihydroxylactone under these conditions is evidence in favour of its formula and also of that proposed for Δ^{α}-angelicalactone. The dihydroxylactones derived from Δ^{β}-angelicalactone and its Δ^{γ}-isomeride,  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{O{-}C{:}CH_2}\end{array}$, should have the formulæ,  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CH_2\cdot CH\cdot OH}\\ \mathrm{O{-}CMe\cdot OH}\end{array}$ and  $\mathrm{CO}{<}\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{O{-}C(OH)\cdot CH_2\cdot OH}\end{array}$ respectively, and the corresponding acids of the salts produced from these by the action of alkali hydroxides would be the hydroxylævulic acids, $CO_2H\cdot CH_2\cdot CH(OH)\cdot COMe$ and $CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot OH$, both of which, being α-hydroxyketones, ought to reduce the silver solution.

G. T. M.

[Phenyl Δ^{α}-Crotonolactone]. The Unsaturated Δ^{α}-Lactone of Benzoylpropionic Acid. By JOHANNES THIELE and N. SALZBERGER (*Annalen*, 1901, **319**, 196—211).—*β-Bromo-α-acetoxy-γ-phenylbutyrolactone*,  $CO<\begin{array}{l}CH(OAc)\cdot CHBr\\ O\text{———}CHPh\end{array}$, prepared from the corresponding hydroxylactone by the action of acetic anhydride, crystallises from alcohol in colourless, vitreous, monoclinic prisms, and melts at 64·5°.

Phenyl Δ^{α}-crotonolactone,  $CO<\begin{array}{l}CH:CH\\ O\text{—}CHPh\end{array}$, obtained from the preceding compound by the action of a copper-zinc couple suspended in cold water, is a yellowish-red oil which solidifies in a freezing mixture, and when warmed with acetic anhydride or an alcoholic solution of piperidine or even on distillation at 140° under 30 mm. pressure, changes into its solid isomeride phenyl-Δ^{β}-crotonolactone,  $CO<\begin{array}{l}CH_2\cdot CH\\ O\text{——}CPh\end{array}$, melting at 91° (compare Fittig, Abstr., 1898, i, 196, and Kugel, *ibid.*, 198). A slow transformation occurs even when the labile Δ^{α}-compound is kept in the dark but the change is not complete even at the end of twelve months. The Δ^{α}-lactone, when hydrolysed either with mineral acids or alkali hydroxides, yields β-benzoylpropionic acid (m. p. 115—116°), and on oxidation with potassium permanganate in the presence of magnesium sulphate gives rise to αβ-dihydroxy-γ-phenylbutyrolactone (Fischer and Stewart, Abstr., 1892, 1447), whilst the Δ^{β}-isomeride furnishes the red compound obtained by Kugel (*loc. cit.*) by the action of ferric chloride.

α-Acetoxy-γ-phenylcrotonic acid, $CHPh:CH\cdot CH(OAc)\cdot CO_2H$, a bye-product in the preparation of phenyl Δ^{α}-crotonolactone, crystallises from water in colourless needles containing $1H_2O$, and melting at 78—79°; the anhydrous acid, obtained by drying the monohydrate over concentrated sulphuric acid, melts at 90—91°, and rapidly regains its water of crystallisation on exposure to the atmosphere. The acid, when treated with a chloroform solution of bromine, yields the dibromide (m. p. 206°; compare Abstr., 1899, i, 611), and on boiling with hydrochloric acid gives rise to β-benzoylpropionic acid; it decomposes into acetic acid and phenyl Δ^{β}-crotonolactone on distillation in a vacuum, a small amount of the Δ^{α}-isomeride being obtained by rapid heating.

α-Chloro-βγ-dibromo-γ-phenylbutyronitrile, $CHPhBr\cdot CHBr\cdot CHCl\cdot CN$, produced by treating the dibromide of cinnamaldehyde cyanohydrin with phosphorus pentachloride, crystallises from alcohol in colourless needles which melt somewhat indefinitely at 110—120°; when mixed with zinc dust and glacial acetic acid, it yields *phenylcrotononitrile*, $CHPh:CH\cdot CH_2\cdot CN$ or $CH_2Ph\cdot CH:CH\cdot CN$, a substance crystallising from light petroleum in leaflets melting at 59—60° and rapidly reducing ammoniacal silver nitrate.

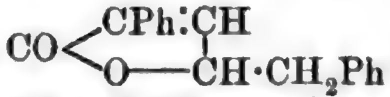
βγ-Dibromo-α-acetoxy-γ-phenylbutyronitrile,

$CHPhBr\cdot CHBr\cdot CH(OAc)\cdot CN$,

formed from the corresponding hydroxy-compound by the action of acetic anhydride, crystallises from alcohol in colourless, four-sided plates and melts at 166—167°. G. T. M.

Unsaturated Lactones of Dihydrocornicularic Acid. By JOHANNES THIELE and FRITZ STRAUS (*Annalen*, 1901, 319, 211—225. Compare Abstr., 1899, i, 612, 614).—*βγ-Dibromo-αδ-diphenylvaleric acid*, $CH_2Ph\cdot CHBr\cdot CHBr\cdot CHPh\cdot CO_2H$, prepared from αδ-diphenyl-Δ^{β}-pentenoic acid and an acetic acid solution of bromine, crystallises from carbon disulphide in white needles melting at 172°. The bromine atoms are readily removed by the action of zinc dust and glacial acetic acid.

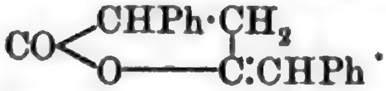
α-Phenyl-γ-benzyl-Δ^{α}-crotonolactone,



$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{CPh{:}CH}\\ \mathrm{O{-}{-}CH\cdot CH_2Ph}\end{array}\right.$

, obtained by treating the preceding dibromide with cold dilute sodium hydroxide solution, crystallises from methyl alcohol in thick, white needles and melts at 91°. The lactone is not affected by hydrogen bromide dissolved in glacial acetic acid, alcoholic hydrochloric acid, or hot acetic anhydride; it immediately reduces ammoniacal silver nitrate, and develops a deep yellow coloration with alcoholic potassium hydroxide solution. Dihydrocornicularic acid is obtained by boiling the lactone either with potassium hydroxide in methyl alcohol, or with a dilute alcoholic solution of sodium carbonate; by the former process, a small amount of a dimeric phenylbenzylcrotonolactone is simultaneously produced; this compound crystallises in lustrous prisms melting at 193°.

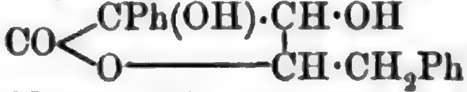
Dihydrocornicularic acid is identical with the product obtained by Spiegel (Abstr., 1882, 1077). This substance, according to the authors' experiments, is reconverted into the original lactone when heated at 200°; Spiegel, on the contrary, obtained a different compound, dihydrocornicularolactone, to which he ascribed the formula



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{CHPh\cdot CH_2}\\ \mathrm{O{-}{-}{-}C{:}CHPh}\end{array}\right. .$$

The polymeric lactone also yields the acid on treatment with potassium hydroxide in methyl alcohol; it reduces ammoniacal silver nitrate, but is not oxidised by alkaline solutions of permanganate.

αβ-Dihydroxy-α-phenyl-γ-benzylbutyrolactone,



$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{CPh(OH)\cdot CH\cdot OH}\\ \mathrm{O{-}{-}{-}{-}CH\cdot CH_2Ph}\end{array}\right. ,$$

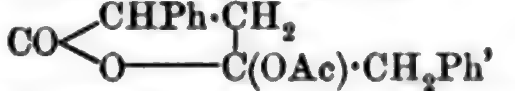
results from the oxidation of α-phenyl-γ-benzyl-Δ^{α}-crotonolactone with potassium permanganate solution; it crystallises from chloroform in white needles and melts at 138°; its *diacetyl* derivative forms lustrous prisms and melts at 137°.

αβγ-Trihydroxy-αδ-diphenylvaleric acid,

$CH_2Ph\cdot CH(OH)\cdot CH(OH)\cdot CPh(OH)\cdot CO_2H$,

obtained in the form of its *barium* salt by hydrolysing the dihydroxylactone with barium hydroxide solution, is unstable and regenerates the lactone. The *silver* salt, $C_{17}H_{17}O_5Ag$, is a hygroscopic, amorphous, white precipitate.

γ-Acetoxy-α-phenyl-γ-benzylbutyrolactone,



$$CO<\begin{matrix}CHPh\cdot CH_2\\ O\text{———}C(OAc)\cdot CH_2Ph\end{matrix}$$

produced from dihydrocornicularic acid by the action of acetic anhydride and sulphuric acid, melts at 105—106° and not at 98—99° as recorded by Spiegel. Dihydrocornicularolactone is formed during the crystallisation of the acetoxy-compound and is obtained in larger quantities by treating the acid with half its weight of acetic anhydride and a trace of an acid; it is converted into its isomeride α-phenyl-γ-benzyl-Δ^a-crotonolactone by heating with a glacial acetic acid solution of hydrogen bromide, but this transformation is not affected by acetic anhydride.

A *lactone*, $C_{17}H_{14}O_2$, isomeric with dihydrocornicularolactone, is produced together with this lactone and its acetyl derivative by heating dihydrocornicularic acid with acetic anhydride, traces of phenylbenzyl-Δ^a-crotonolactone are also obtained; it crystallises from alcohol in highly refractive leaflets and melts at 128·5°. The new lactone is probably a stereoisomeride of dihydrocornicularolactone, and resembles the latter in reducing ammoniacal silver nitrate rapidly, but not instantaneously, and in developing a yellow coloration with alcoholic potassium hydroxide; it regenerates dihydrocornicularic acid by alkaline hydrolysis. G. T. M.

Naphthaldehydic Acid. By JOSEF ZINK (*Monatsh.*, 1901, 22, 986—990).—When naphthaldehydic acid is formed by fusing acenaphthenequinone with potash, it is accompanied by naphthalic acid, the amount of the latter increasing with the duration of the fusion. Naphthalic acid is also formed on boiling naphthaldehydic acid with alkalis. The formation of a hydroxy-acid or lactone corresponding with phthalide could not be detected. Potassium cyanate in absolute alcohol has the same action as aqueous alkalis.

Methyl naphthaldehydate melts at 105° (compare Wegscheider, *Monatsh.*, 1882, 348). G. Y.

New Glyceride: Glyceryl Phthalate. By WATSON SMITH (*J. Soc. Chem. Ind.*, 1901, 20, 1075—1076).—When glycerol and phthalic anhydride are heated for a long time nearly to boiling, either alone or with zinc chloride, the product is a solid mass resembling glass slag in appearance, which is most probably *diglyceryl triphthalate*. It is practically insoluble in all solvents, with the exception of acetone, in which it dissolves to a slight extent. On hydrolysis with sodium hydroxide, it yields glycerol and phthalic acid; with sulphuric acid, it gives sulphonated products, and it is nitrated by a mixture of concentrated nitric and sulphuric acids. H. R. LE S.

Derivatives of Nitrophthalic Acid. By HEINRICH SEIDEL (*Ber.*, 1901, 34, 4351—4353. Compare Onnertz, this vol., i, 95).—β-Nitrophthalic acid yields *β-nitrophthalimide* when heated in gaseous ammonia; this crystallises in yellowish leaflets melting at 202°; *α-nitrophthalimide* forms yellowish needles melting at 216°. From the α-imide, by means of Hofmann's reaction, 6-*nitro-2-aminobenzoic acid*,

$NO_2\cdot C_6H_3(NH_2)\cdot CO_2H$, is obtained as an ochre-yellow, crystalline powder melting at 184°; the acid readily loses carbon dioxide, with formation of *m*-nitroaniline. The β-imide yields two isomerides, *4-nitro-2-aminobenzoic acid* melting at 264° and *5-nitro-2-aminobenzoic acid* melting at 280°. From the former, 4-nitrosalicylic acid (m. p. 235°) and 4-aminosalicylic acid (m. p. 220° with decomposition) can be obtained. The two nitrophthalic acids are reduced by sodium sulphide to *aminophthalic acids*; the α-amino-acid is a yellow powder melting at 226°, whilst the β-amino-acid crystallises in needles, which lose their crystalline form on drying and melt at 280°. K. J. P. O.

α-Phenylglutaric Acid and γδ-Diphenylallylacetic Acid [γδ-Diphenyl-γ-pentenoic Acid]. By FRITZ FICHTER and OTTO MERCKENS (*Ber.*, 1901, **34**, 4174—4178).—*Ethyl γ-acetyl-α-phenylglutarate*, $CO_2Et\cdot CHAc\cdot CH_2\cdot CHPh\cdot CO_2Et$, obtained by condensing ethyl chlorohydratropate (Spiegel, Abstr., 1881, 277) with ethyl sodioacetoacetate, boils at 189° under 11 mm. pressure, and, on hydrolysis with 25 per cent. alcoholic potassium hydroxide, yields α-phenylglutaric acid; the latter is also obtained by heating with hydrochloric acid *ethyl α-phenylpropane-ααγ-tricarboxylate*, which is formed by condensing ethyl β-iodopropionate with ethyl phenylmalonate, and boils at 219—221° under 13 mm. pressure.

α-Phenylglutaric acid is best purified in the form of its *calcium* salt, which crystallises in white, microscopic needles with $4H_2O$; the *barium* salt, with $2H_2O$, is ill-defined, the *zinc* salt, with $7H_2O$, forms sheaves of needles, and the *silver* salt is anhydrous. The pure *acid* separates from benzene or light petroleum in small crystals, melts at 82—83°, and partially changes in dry air into the anhydride; the latter is obtained quantitatively on distilling the acid under reduced pressure and crystallises from ether in beautiful, small needles, melts at 95°, and boils at 218—230° under 13 mm. pressure. On boiling the anhydride with water, a hydrated form (with $1H_2O$) of α-phenylglutaric acid is obtained in large, colourless needles.

When dry sodium α-phenylglutarate is heated with benzaldehyde (1 mol.) and acetic anhydride for 50 hours at 155°, considerable quantities of *γδ-diphenylallylacetic acid* [*γδ-diphenyl-γ-pentenoic acid*], $CHPh\colon CPh\cdot CH_2\cdot CH_2\cdot CO_2H$, are formed; it is best isolated in the form of the sparingly soluble, amorphous *calcium* salt (with $1\frac{1}{2}$—$2H_2O$); the *barium* salt contains $2H_2O$. The pure *acid* crystallises from a mixture of ether and light petroleum in colourless needles, melts at 106°, and when treated with hydrogen bromide in glacial acetic acid at the ordinary temperature, yields an *oil* which is readily transformed into *γδ-diphenylvalerolactone*; this separates from ether in beautiful crystals and melts at 59—60°. W. A. D.

Anhydrous Methyl Gallate. By GIROLAMO MAZZARA (*Gazzetta*, 1901, **31**, ii, 347—356).—Whilst ethyl gallate crystallises with $2\frac{1}{2}H_2O$, it has been stated by Biétrix (Abstr., 1893, i, 343) that the methyl compound contains $3H_2O$. In this case, then, there appears to be no analogy similar to that existing between the methyl and ethyl esters of the dihalogenated gallic acids, which all crystallise with

$1\frac{1}{2}H_2O$. The author finds, however, that when the anhydrous methyl gallate described by Will (Abstr., 1888, 1059) is crystallised several times from water it contains $1\frac{1}{4}H_2O$; this hydrate, which he assumes to be a compound of the anhydrous ester with the hydrate containing $2\frac{1}{2}H_2O$, readily reverts to the anhydrous form. Ethyl gallate melts at 158° if crystallised from benzene, or at 155° if it is crystallised from water (with $2\frac{1}{2}H_2O$) and dehydrated. T. H. P.

Action of Bromine on Methyl and Ethyl Gallates and on their Chloro-derivatives. By P. Guarnieri (*Gazzetta*, 1901, **31**, ii, 356—363).—Ethyl dibromogallate crystallises with $1\frac{1}{2}H_2O$ and melts at 137°. Methyl dibromogallate, which Biétrix (Abstr., 1893, i, 343) described as crystallising with $1H_2O$ and melting at 139°, is found by the author to contain $1\frac{1}{2}H_2O$ and to melt at 169°.

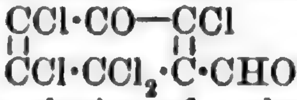
Ethyl Chlorobromogallate, $C_6H_2BrCl(OH)_3{\cdot}CO_2Et$ [$Cl : Br : (OH)_3 = 2 : 6 : 3 : 4 : 5$], prepared by the action of bromine on ethyl chlorogallate in acetic acid solution, separates from water in leaflets containing $1\frac{1}{2}H_2O$, and melting, after dehydration, at 134—135°. *Methyl chlorobromogallate* crystallises from water in yellow leaflets containing $1\frac{1}{2}H_2O$, and melting after dehydration at 162—163°.

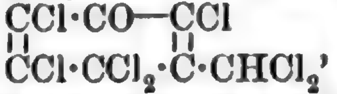
All the halogenated methyl and ethyl esters of gallic acid melt at lower temperatures than the esters from which they are derived; the disubstituted derivatives of methyl and ethyl gallates crystallise with $1\frac{1}{2}H_2O$, whilst the monohaloid compounds contain only $1H_2O$. The methyl esters in all cases melt at higher temperatures than the corresponding ethyl compounds. T. H. P.

Interaction of Tannin and Tartar Emetic. By Nicolai N. Ljubavin (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 680—684).—The author has studied the action taking place when solutions of tannin and tartar emetic are mixed under different conditions of concentration and in presence of ammonia and of sodium acetate. The action is found to depend on the order in which the two solutions are mixed; thus, when a 1 per cent. solution of tannin (2—3 mols.) is added to 1 per cent. tartar emetic solution (1 mol.), a precipitate is obtained, whilst if the solutions are mixed in the inverse order, no precipitate is formed. The precipitate obtained is in every case white and gelatinous, giving greyish lumps when dried in a desiccator. When dried at the ordinary temperature, the composition corresponds with the formula $C_{14}H_9(SbO)O_9,H_2O$, but if dried at 100° the formula is$C_{14}H_9SbO_9$. The filtrate from the precipitate always gives the reactions for antimony and for tannin. T. H. P.

Action of Benzenediazonium Chloride on Methylenedi-2-hydroxy-3-naphthoic Acid. By Erich Strohbach (*Ber.*, 1901, **34**, 4162—4165. Compare Möhlau and Strohbach, Abstr., 1900, i, 368).—The basic *sodium* salt, $CH_2[C_{10}H_5(ONa){\cdot}CO_2Na]_2,2H_2O$, of methylenedi-2-hydroxy-3-naphthoic acid, obtained by treating the acid with an alcoholic solution of sodium ethoxide, crystallises in pale yellow needles.

The methylene radicle of methylenedi-2-hydroxy-3-naphthoic acid is displaced by two azo-residues when benzenediazonium chloride is added to an alkaline solution of the acid, the product being identical with von Kostanecki's 1-benzeneazo-2-hydroxy-3-naphthoic acid (Abstr., 1894, i, 91). G. T. M.

Chlorination of *m*-Hydroxybenzaldehyde. By HEINRICH BILTZ and OTTO KAMMANN (*Ber.*, 1901, **34**, 4118—4128. Compare Zincke and Walbaum, Abstr., 1891, 708).—*Aldehydotrichloroquinodichloride*,  $\begin{array}{l} CCl\cdot CO—CCl \\ \| \qquad\qquad \| \\ CCl\cdot CCl_2\cdot C\cdot CHO \end{array}$, prepared by saturating with chlorine an acetic acid solution of *m*-hydroxybenzaldehyde slightly diluted with water, first at the ordinary temperature and then on the water-bath, crystallises from glacial acetic acid in yellow plates, and melts at 137—138°. It is decomposed by alkali hydroxides and carbonates, and also by phenylhydrazine and aniline. The *oxime*, $C_7H_2O_2NCl_5$, crystallises from dilute alcohol in brownish-yellow leaflets, melts at 169°, and is readily soluble in the ordinary organic solvents. The *semicarbazone* separates in orange-coloured, cubical crystals, and melts at 202°.

Dichloromethyltrichloroquinodichloride,  $\begin{array}{l} CCl\cdot CO—CCl \\ \| \qquad\qquad \| \\ CCl\cdot CCl_2\cdot C\cdot CHCl_2 \end{array}$, produced by treating the preceding aldehyde with phosphorus pentachloride, separates in colourless crystals and melts at 117°; a bye-product containing phosphorus and melting at 224° is also formed in this reaction.

Tetrachloro-m-*hydroxybenzaldehyde*, $OH\cdot C_6Cl_4\cdot CHO$, obtained in quantitative yield by reducing aldehydotrichloroquinodichloride in acetic acid solution with stannous chloride, crystallises from benzene in colourless needles melting at 189—190°. The *acetyl* derivative, $OAc\cdot C_6Cl_4\cdot CHO$, crystallises from glacial acetic acid in needles, and melts at 112°.

Tetrachloro-m-*hydroxybenzaldehydephenylhydrazone*,

$$OH\cdot C_6Cl_4\cdot CH\colon N\cdot NHPh,$$

produced by mixing its generators in acetic acid solution, separates from this solvent in felted, yellow needles and melts at 124—125°. Both the phenylhydrazone and the aldehyde dissolve in solutions of the alkali carbonates and hydroxides, developing yellow colorations.

Acetyltetrachloro-*m*-hydroxybenzaldehyde, when treated with phenylhydrazine, yields the corresponding *phenylhydrazone*,

$$OAc\cdot C_6Cl_4\cdot CH\colon N\cdot NHPh,$$

a substance crystallising in yellow plates and melting at 188—189°, which, on warming with acetic anhydride, gives rise to the *diacetate*, $OAc\cdot C_6Cl_4\cdot CH\colon NPhAc$; this compound, also obtained by acetylating tetrachloro-*m*-hydroxybenzaldehydephenylhydrazone, crystallises in light brown leaflets, and melts at 148°.

Tetrachloro-m-*ethoxybenzaldehyde*, $OEt\cdot C_6Cl_4\cdot CHO$, prepared by boiling together tetrachloro-*m*-hydroxybenzaldehyde, sodium ethoxide, and ethyl iodide in alcoholic solution, separates from glacial acetic acid in felted, colourless needles, and melts at 67—68°; the *phenylhydrazone* crystallises from the ordinary organic solvents in yellow leaflets melting at 111—112°.

Tetrachloro-m-*hydroxybenzaldoxime*, $OH\cdot C_6Cl_4\cdot CH\colon NOH$, produced from hydroxylamine hydrochloride, sodium hydroxide, and the corresponding aldehyde in aqueous solution, crystallises from benzene in white needles and melts at 194—195°.

*Acetyltetrachloro-*m*-hydroxybenzonitrile*, $OAc\cdot C_6Cl_4\cdot CN$, obtained by heating the preceding oxime with acetic anhydride, crystallises in aggregates of lustrous, pale red needles and melts at 145—146°; when hydrolysed with a boiling alcoholic solution of sodium ethoxide, it yields the sodium derivative of *tetrachloro-*m*-hydroxybenzonitrile*. The latter nitrile forms yellowish-white needles and melts at 219—220°.

*Tetrachloro-*m*-hydroxybenzamide*, $OH\cdot C_6Cl_4\cdot CO\cdot NH_2$, produced by hydrolysing tetrachloro-*m*-hydroxybenzonitrile with 10 per cent. hydrochloric acid at 200°, crystallises from glacial acetic acid in needles melting at 260—261°; on further treatment with boiling 50 per cent. sulphuric acid, the amide yields tetrachloro-*m*-hydroxybenzoic acid (m. p. 172°), this acid being also obtained by the direct oxidation of tetrachloro-*m*-hydroxybenzaldehyde.

*Tetrachloro-*m*-hydroxybenzylidene chloride*, $OH\cdot C_6Cl_4\cdot CHCl_2$, prepared by the action of phosphorus pentachloride on tetrachloro-*m*-hydroxybenzaldehyde, crystallises from glacial acetic acid in prisms with truncated, pyramidal ends, and melts at 86—87°; it separates from the dilute acid in aggregates of needles containing $3H_2O$ and melting at 66—68°. This chloride is also obtained by reducing dichloromethyltrichloroquinodichloride with stannous chloride, and justifies the constitution given to this quinone derivative.

*Tetrachloro-*m*-acetoxybenzylidene chloride*, $OAc\cdot C_6Cl_4\cdot CHCl_2$, produced by warming the preceding compound with acetic anhydride, crystallises from glacial acetic acid in colourless, double pyramids. G. T. M.

Halogen Derivatives of Phenols. By W. Richter (*Ber.*, 1901, **34**, 4292—4296. Compare Auwers, Abstr., 1899, i, 36; 1900, i, 164, 165).—p-*Acetoxybenzylidene bromide*, $CHBr_2\cdot C_6H_4\cdot OAc$, obtained by the action of phosphorus pentabromide on *p*-acetoxybenzaldehyde (b. p. 264—265°), crystallises from light petroleum in colourless prisms, melts at 97—98°, and is readily soluble in most organic solvents. It turns dark on exposure to light, and on treatment with an acetic acid solution of hydrogen bromide, even in the entire absence of moisture, yields *p*-hydroxybenzaldehyde. By the action of bromine in chloroform solution, it is converted into dibromo-*p*-hydroxybenzaldehyde.

m-*Acetoxybenzylidene bromide*, obtained by the action of phosphorus pentabromide on a chloroform solution of *m*-acetoxybenzaldehyde (b. p. 263°), is a yellow oil, which on treatment with hydrogen bromide yields *m*-hydroxybenzaldehyde; bromine transforms it into tribromo-*m*-hydroxybenzaldehyde.

The constitution of Auwers and Hampe's tetrabromotoluquinol (Abstr., 1899, i, 96) has been confirmed by the preparation of a *diacetyl* derivative melting at 282—283° and by its reduction to tribromotoluquinone melting at 203—204°.

Tetrachlorotoluquinone (Gorup, *Annalen*, 1867, **143**, 159) melts at 266—270°, and on reduction with sulphurous acid yields the corresponding *quinol*, $CH_2Cl\cdot C_6Cl_3(OH)_2$; this crystallises from acetic acid in glistening plates, melts at 228°, and is readily soluble in dilute alkalis.

The chlorine of the side chain is not readily replaceable. The *diacetate* crystallises in glistening needles melting at 232° and readily soluble in acetone. J. J. S.

New Reactions of Organo-metallic Compounds. Synthesis of Ketones.

By EDMOND E. BLAISE (*Compt. rend.*, 1901, **133**, 1217—1218. Compare Abstr., 1901, i, 252, 317, 363).—The crystalline compounds of the type $CRR'{:}N\cdot MgI,Et_2O$ (*loc. cit.*), which are formed when nitriles interact with the compounds of magnesium alkyl iodides and ether, react with water yielding ketones. To prepare the ketones, it is not necessary to isolate the intermediate compounds; the nitrile (1 mol.) is added to a solution in dry ether of magnesium alkyl iodide (1·5 mols.); the mixture is heated at 100°, and then, after addition of water and the distillation of the ether, the ketone is distilled in a current of steam. The best yields are obtained with aromatic nitriles, in which the cyano-group is in the nucleus.

o-*Tolyl ethyl ketone*, $C_6H_4Me\cdot COEt$, is a liquid boiling at 219—221°; its *semicarbazone* melts at 173°. *Benzyl* n-*propyl ketone*, prepared from butyronitrile and benzyl chloride, is a liquid, having the odour of aniseed, and boiling at 238—241°; its *semicarbazone* melts at 84°. *Benzyl* iso*amyl ketone* boils at 267°; its *semicarbazone* melts at 133°. o-*Methyldeoxybenzoin* boils at 317—320° under the ordinary pressure and at 191° under 21 mm. pressure; its *semicarbazone* melts at 198°. p-*Tolyl butyl ketone* melts at 22° and boils at 266—267°; its *semicarbazone* melts at 212°. p-*Tolyl propyl ketone* boils at 248—250°; its *semicarbazone* melts at 232°. n-*Propyl* iso*amyl ketone* boils at 176—178°; its *semicarbazone* melts at 102°. Ethyl propyl ketone and phenyl ethyl ketone have also been prepared by this method; their *semicarbazones* melt at 110° and 182° respectively. K. J. P. O.

Condensation of Acetylene Hydrocarbons with Alkyl Esters. Synthesis of Acetylenic Ketones and β-Ketonic Esters.

By CHARLES MOUREU and RAYMOND DELANGE (*Compt. rend.*, 1902, **134**, 45—47).—*Butyrylphenylacetylene*, $COPr\cdot C⋮CPh$, a liquid of sp. gr. 0·998 at 0° and boiling at 135—137° under 9 mm. pressure, is obtained by the action of amyl butyrate on the sodium derivative of phenylacetylene in presence of ether, and treatment of the product by water. When hydrolysed with sulphuric acid, it yields the β-diketone, *benzoylbutyrylmethane* (*phenyl propyl methylene diketone*), the copper derivative of which crystallises from alcohol in prisms melting at 132—133°. *Benzoylphenylacetylene*, $COPh\cdot C⋮CPh$, which melts at 49·5° and boils at about 200° under 15 mm. pressure, is obtained similarly from ethyl benzoate and phenyl acetylene; when hydrolysed, it yields dibenzoylmethane, melting at 81°.

The alkyl esters of β-ketonic acids are readily obtained by the action of ethyl, *iso*propyl, *iso*butyl, and amyl acetates and amyl butyrate on the sodium derivative of heptylidene. iso*Propyl acetoacetate* boils at 75° under 15 mm. pressure, and its copper derivative melts at 175°; *amyl butyrylbutyrate* boils at 125—127° under 9 mm. pressure.

According to the author, a complex sodium derivative such as $OEt\cdot CPh(ONa)\cdot C⋮CPh$ is first formed, and this, in contact with water, yields the acetylenic ketone, alcohol, and sodium hydroxide. In the case of β-ketonic esters a still more complex disodio-derivative is the first product (compare Abstr., 1901, i, 581 and 442). C. H. B.

Cotoin. By JACQUES POLLAK (*Monatsh.*, 1901, **22**, 996—1001).—Cotoin yields a mononitroso-derivative and has therefore the constitution $COPh\cdot C_6H_2(OH)_2\cdot OMe$ [COPh : OH : OH : OMe = 1 : 2 : 6 : 4], and not [1 : 2 : 4 : 6], since, according to the observations of Kostanecki (*Ber.*, 1887, **20**, 3133), a substance with the latter formula should yield a dinitroso-derivative.

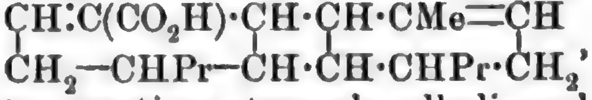
Nitrosocotoin crystallises from acetic acid in dark red leaves and in glistening, orange-yellow needles, both forms melting at 153—154°. The needles, which lose weight over sulphuric acid, probably contain acetic acid of crystallisation. G. Y.

Special Case of Steric Hindrance. By ERNST BÖRNSTEIN (*Ber.*, 1901, **34**, 4348—4351).—On treating *p*-toluidino-*p*-toluquinonemonotolylimide, $C_7H_7\cdot NH\cdot C_7H_5O\colon N\cdot C_7H_7$ (Abstr., 1901, i, 375), with hydroxylamine hydrochloride and sodium carbonate in the presence of alcohol, a reaction takes place in which the group (:NOH) replaces the group $C_7H_7N\colon$, and *p*-toluidine and the *mono-oxime* of *p*-toluidino-*p*-toluquinone, $C_7H_7\cdot NH\cdot C_7H_5O\colon NOH$, are formed. The oxime crystallises in yellowish-red, lustrous leaflets melting at 190°, soluble in alkali hydroxides and carbonates. Concentrated hydrochloric acid dissolves it with a bluish-violet coloration, and concentrated sulphuric acid with a green coloration which becomes violet on the addition of water. K. J. P. O.

Borneol- and Menthol-glycuronic Acids. By A. BONANNI (*Beitr. chem. Physiol. Path.*, 1901, **1**, 304—309).—See this vol., ii, 160.

Colophony. By WILHELM FAHRION (*Zeit. angew. Chem.*, 1901, **14**, 1197—1208, 1221—1233, 1252—1253).—The colophony used was of American origin. The acid number obtained was 170·2, the saponification number 177·9, the difference (7·7) being the ether number.

Colophony is partially soluble in light petroleum, and the author understands by "inner acid or saponification number" the quantity of potassium hydroxide, expressed in milligrams, required for the neutralisation or saponification of 1 gram of the soluble portion. The numbers obtained were 162·7 and 164·3 respectively; whilst in another series, the "inner saponification number" was 165·2. The inconstancy of this leads to the conclusion that the portion of colophony soluble in light petroleum does not contain an ester, but another neutral saponifiable substance.

The part insoluble in light petroleum consists essentially of an acid, which, however, in presence of excess of alkali unites with more of this than is necessary for the saturation of the carboxyl group. The amount of insoluble residue (in light petroleum) depends on the extent to which the colophony has suffered autoxidation. The colophony also contains unsaponifiable matter, so that the molecular weight of the acid cannot be calculated directly from the "inner acid number"; the quantity of unsaponifiable matter increases with the length of time that the colophony is exposed to the air. After determining the percentage of acid in the portion soluble in light petroleum, the molecular weight calculated from the "inner acid number" is about 313. This agrees with the formula $C_{20}H_{30}O_2$ for sylvic acid. It is proved that crystallised sylvic acid is identical with abietic acid, and Mach's formula, $C_{19}H_{28}O_2$, is incorrect. The melting point of crystallised sylvic acid varies considerably (148° to 164°) according to the method of heating. The constitution suggested by Bischoff and Nastvogel, namely,  $\begin{array}{l} \text{CH:C(CO}_2\text{H)·CH·CH·CMe=CH} \\ \text{CH}_2\text{—CHPr—CH·CH·CHPr·CH}_2 \end{array}$, seems to satisfactorily express its reactions towards alkali and iodine respectively. The sylvic acid contained in the colophony is in an amorphous condition, and from the fact that crystallised sylvic acid gives an ethyl ester, it is probable that the above constitution represents the amorphous variety, and in the crystallised the carboxyl group lies further away from the doubly linked carbon atoms. From the amorphous sylvic acid, the crystallised modification can be obtained by treatment with aqueous alcohol or by the action of hydrochloric acid on the alcoholic solution. The melting point of the amorphous acid is not very definite, but lies considerably below that of the crystallised. By prolonged heating of the crystallised acid, it is converted into the amorphous variety, and at the same time the molecular weight (calculated from the acid value) is increased because some other products are formed; in fact, colophony is produced, and this leads to the view that the turpentine contains sylvic acid, and as the terpenes only distil at a comparatively high temperature, this serves to convert the acid into colophony.

Sylvic acid is autoxidisable; a peroxide, $C_{20}H_{30}O_6$, is formed, and this is transformed by intramolecular rearrangement into *tetraoxysylvic acid*, $C_{20}H_{28}(OH)_2O_4$. The autoxidation, however, takes place in stages, and a peroxide of the formula $C_{20}H_{30}O_4$ is first produced, which is transformed into *dioxysylvic acid*, $C_{20}H_{29}(OH)O_3$.

The part of the colophony insoluble in light petroleum contains these peroxides. When oxidised with permanganate in alkaline solution, sylvic acid gives an acid which is probably *tetrahydroxysylvic acid*, $C_{20}H_{32}(OH)_4O_2$.

Incidentally, the author has investigated the iodine value of certain phenols, quinones, and peroxides, and concludes that for these it is quite worthless, and for substances in general containing hydroxyl groups its value is always doubtful. J. McC.

The Resins of Copaiva Balsams. By [ALEXANDER TSCHIRCH and] EDUARD KETO (*Arch. Pharm.*, 1901, **239**, 548—581).—Copaiva balsams from Maracaibo and Para were examined; also an African variety, illurin balsam, obtained from *Hardwickia Mannii* in the Niger basin. The balsam was diluted with ether, and extracted completely with 5 per cent. aqueous sodium carbonate, and then a few times with 1 per cent. aqueous potassium hydroxide. From the residue, the ether was distilled off, and the *essential oil* distilled over with steam; there remained a mixture of indifferent *resens*, mostly, but not wholly, soluble in alcohol. These are present in but small amount, whereas the oil forms the chief constituent of the balsam.

The resin acids were liberated from the sodium carbonate solution with hydrochloric acid, and redissolved in ether; the solution was extracted first with 5 per cent. aqueous ammonium carbonate, then with 5 per cent. aqueous sodium carbonate. In the case of the Para balsam, there were obtained: from the ammonium carbonate solution, *paracopaivic acid*, $C_{20}H_{32}O_3$, melting at 145—148°, and from the sodium carbonate solution, *homoparacopaivic acid*, $C_{18}H_{28}O_3$, melting at 111—112°. From samples of Maracaibo balsam, *β-metacopaivic acid*, $C_{11}H_{16}O_2$ (or $C_{16}H_{24}O_3$ or $C_{22}H_{32}O_4$), melting at 89—90°, and *illuric acid*, $C_{20}H_{28}O_3$, melting at 128—129°, were obtained. From illurin balsam, illuric acid was obtained. The amount of the resin acids varies from 10 per cent. of the balsam in the case of the Para variety to 30—40 per cent. in the case of that from Maracaibo. In the case of the Para balsam, about equal amounts of the acids dissolve in the ammonium and sodium carbonate solutions; in the other cases but little dissolved in the ammonium carbonate. Only a small part of the acids could be obtained crystalline, the bulk being amorphous and not entirely soluble in light petroleum.

One sample of illurin balsam contained a crystalline sediment consisting of illuric acid; in consequence, this acid could be isolated in comparatively large amount and its properties studied. It crystallises in the hexagonal system and has $[\alpha]_D$ $-58·9°$ in 5 per cent. alcoholic solution at 18°. It is a monobasic acid; its crystalline *barium* (with $4H_2O$?), *sodium* (with $6H_2O$?), and *lead* salts and its amorphous *silver* salt were analysed. It does not contain a methoxyl or ethoxyl group; it will not form an acetyl or benzoyl derivative, or a methyl or ethyl derivative; it will not react with hydroxylamine or phenylhydrazine; with phosphorus pentachloride or triiodide, it does not yield a well defined product; with alcoholic hydrochloric acid, it does not yield an ester, but is transformed into an isomeric *acid*, $C_{20}H_{28}O_3$, melting at 108—109°; it reacts with nitric acid, and also with sulphuric acid, but the respective products do not contain nitrogen or sulphur. The acid has an iodine number corresponding with the presence of two double linkings, and in alcoholic solution it takes up 4 atoms of bromine. It gives the cholesterol reactions and is not affected by fusion with potassium hydroxide; in these and other respects it resembles the resin acids of the *Coniferæ*, especially pimaric acid, but it differs from them in that it reduces silver salts in alkaline solution. It resists the action of reducing agents, but it can be oxidised; excess of alkaline permanganate converts it into carbonic, oxalic, formic, acetic, and other fatty acids, together with a small quantity of an acid which melts at 194°. Illuric acid is probably identical with the acid obtained by Umney and by Peinemann from illurin balsam; possibly, also with Fehling's oxycopaivic acid. Schweitzer-Rose's copaivic and Strauss's metacopaivic acids could not be obtained from the balsam.

A commercial specimen of "copaivic acid" appeared to be identical with metacholestol (Mach, Abstr., 1895, i, 384). C. F. B.

Constituents of Koso Flowers. By [RUDOLF BOEHM and] ARTHUR LOBECK (*Arch. Pharm.*, 1901, **239**, 672—696. Compare Leichsenring, Abstr., 1894, i, 424; Daccomo and Malagnini, Abstr., 1899, i, 158).—By repeated crystallisation from alcohol, commercial kosin was separated into less soluble α-kosin melting at 160°, and a little β-kosin, more soluble in alcohol, and melting at 120°; both have the constitution $C_{21}H_{24}O_5(OMe)_2$ or $C_{20}H_{20}O_5(OMe)_2$. α-Kosin forms a tribenzoyl derivative, $C_{20}H_{17}O_2(OBz)_3(OMe)_2$ or $C_{21}H_{21}O_2(OBz)_3(OMe)_2$; when heated with 10 per cent. aqueous sodium hydroxide and zinc dust, it is attacked, but only slightly, some methylphloroglucinol methyl ether (compare Boehm, Abstr., 1899, i, 32) being formed; when it is heated for a few minutes with strong sulphuric acid, the same product is obtained in 14 per cent. yield, together with butyric acid.

A commercial ethereal extract of *Flores Koso* was examined by pounding it with calcined magnesia, extracting the mixture with water, and precipitating the extract with dilute sulphuric acid. From a solution of the crude product in methyl alcohol, a little *anhydroprotokosin*, $C_{58}H_{74}O_{17}$, crystallised slowly; this melts at 182° and, when crystallised from alcohol containing a little water, is converted into Leichsenring's protokosin, $C_{29}H_{38}O_9$, which contains two methoxyl groups and is thus $C_{27}H_{32}O_7(OMe)_2$. From the mother liquor, by evaporation and treatment with light petroleum, small quantities of *kosidin*, $C_{29}H_{40}O_9(OMe)_2$, melting at 178°, were obtained. The main constituent, however, was kosotoxin, which melted at 62°, and probably has the formula $C_{50}H_{62}O_{18}(OMe)_2$, rather than half this, since all the other constituents of the drug contain 2 methoxyl groups in the molecule. When heated with aqueous sodium hydroxide and zinc dust, kosotoxin is, to a large extent, converted into kosin, but some trimethylphloroglucinol and dimethylphloroglucinol are formed also. When heated with strong sulphuric acid for a little while, it yields some trimethylphloroglucinol and methylphloroglucinol methyl ether.

Different samples and extracts of the flowers were found to differ greatly. From one sample of the flowers, a little of a poisonous substance, *α-kosotoxin*, was obtained, which melts at 68—69° and seems to have the constitution $C_{24}H_{34}O_8(OMe)_2$. From a sample of ethereal extract, a microcrystalline substance was obtained which burns on platinum foil without melting, contains methoxyl, and has the composition $C_{19}H_{12}O_{10}$.

C. F. B.

A Blue Pigment from Crenilabrus Pavo. By Richard von Zeynek (*Zeit. physiol. Chem.*, 1901, **34**, 148—152).—A deep blue pigment can be extracted by means of glycerol from the floats of *Crenilabrus pavo.* Its solubilities and optical properties are described; it is not yet identified chemically.

W. D. H.

Guaiacum Blue and Aloin Red. By Eduard Schaer (*Verh. Natur.-Gesell. Basel*, 1901, **13**, 287—307. Compare Abstr., 1900, i, 512; ii, 583).—Schönbein has suggested that the blue substance formed by oxidising 'guaiaconic acid' from guaiacum resin is a peroxide similar to ozone. In accordance with this view, it is now shown that the blue colour is very readily destroyed by a number of chemical agents and is also sensitive to the action of light. The influence of acids is determined by their strength; sulphuric, hydrochloric, and salicylic acids act the most powerfully, then tartaric, citric, and formic acids, whilst benzoic and acetic acids have only a feeble action; when dissolved in solvents not miscible with water, the blue colour is only very slightly sensitive to the action of acids. Alkali hydroxides and carbonates and alkaline salts act much more vigorously than acids; they quickly destroy the blue colour when formed, and entirely prevent its formation by the oxidation of guaiacum resin or guaiaconic acid. The action of light greatly facilitates the formation of guaiacum blue by the atmospheric oxidation of guaiacum resin or of the acid prepared from it, but it is also very active in bringing about the subsequent spontaneous bleaching of the blue colour; both these processes are regarded as oxidations in which the oxygen of the air is rendered active by the resin and other constituents of the solution.

It is pointed out that the formation of 'aloin-red' from 'barbaloin' proceeds in a manner very similar to that of 'guaiacum-blue' from guaiacum resin, and five methods of producing this red compound are described, including two in which peroxides are probably the active agents; its formation may be used as a very sensitive test for aloe preparations, for cyanogen and halogen compounds (especially hydrocyanic acid), for free ammonia, for copper, and for peroxides.

T. M. L.

Basic Properties of Oxygen. By Paul Walden (*Ber.*, 1901, **34**, 4185—4202. Compare Collie and Tickle, Trans., 1899, **75**, 710; Kehrmann, Abstr., 1900, i, 61; 1901, i, 484; von Baeyer and Villiger, Abstr., 1901, i, 658, and this vol., i, 112; Werner, this vol., i, 50).—The early part of this paper consists of an historical summary; the latter part is a physico-chemical study of dimethylpyrone. This substance has no appreciable influence on the speed of mutarotation of sucrose; if a base, it is a very much weaker one than aniline. The values for the distribution ratios between benzene and water, of picric acid alone, and of picric acid along with dimethylpyrone (1 mol.) show that in concentrated solutions ($v=32$) a dimethylpyrone picrate is formed which is decomposed into its constituents by dilution. From the difference in the depression of the freezing point of dilute solutions of hydrochloric acid caused by the addition of dimethylpyrone, the affinity constant, k_b, of the latter as a base is found to be approximately 3×10^{-14}.

Dimethylpyrone comports itself as a relatively good electrolyte in liquid sulphur dioxide at 0°; the conductivity increases on dilution, owing, probably, to dissociation of the salt formed into the ions $\overset{-\,-}{SO_2}$ and $\overset{+\,+}{C_7H_8}O_2$. Both dimethylpyrone and tribromoacetic acid are very feeble conductors when dissolved separately in acetonitrile, but the combination of the two in molecular proportions in concentrated solution has a considerable conductivity. Formation of a salt obviously occurs, but the rapid diminution of conductivity with dilution indicates that it has little stability. The conductivity of dimethylpyrone in aqueous solution is very slight; $\mu_D=202$ at 25° approximately, and $k=7\cdot5 \times 10^{-9}$.

From measurements of the conductivity of aqueous solutions of picric acid at 25°, and of aqueous solutions of picric acid (1 mol.) + dimethylpyrone (1 mol.) diluted (1) with water, (2) with an *N*/64 solution of dimethylpyrone, the affinity constant, k_b, of dimethylpyrone, as a base was found to be $2{\cdot}4 \times 10^{-14}$, a value agreeing closely with that obtained by the freezing point method (*supra*). Dimethylpyrone is thus stronger than carbamide and much weaker than aniline. The influence of dimethylpyrone on the conductivity of aqueous solutions of sodium hydroxide shows that it is not only a base but also an acid with an affinity constant $k_s = 0{\cdot}88 \times 10^{-14}$; it is therefore of an amphoteric character, and capable of forming both hydrogen and hydroxyl ions. The high value of k obtained with aqueous solutions of dimethylpyrone corresponds in reality to the formation of an "internal salt." W. A. D.

Oxygen Bases. By JAMES WALKER (*Ber.*, 1901, **34**, 4115—4118. Compare Baeyer and Villiger, Abstr., 1901, i, 658).—In order to ascertain the strength of the oxygen bases, dimethylpyrone and tetramethylpyrone, each of these compounds was dissolved in the equivalent amount of *N*/10 hydrochloric acid, and 20 c.c. of the solution were mixed with 1 c.c. of methyl acetate in a thermostat at 35°. The course of the hydrolysis was followed by titrations with standard barium hydroxide solution, and a comparative experiment was made with carbamide. The calculated velocity coefficient showed that these bases have approximately the same strength, the values of the constant for carbamide, dimethylpyrone, and tetramethylpyrone being 0·00066, 0·00065, and 0·00068 respectively. The hydrolytic experiments carried out in dilute solutions of varying concentration show that the hydrochlorides of carbamide and dimethylpyrone are dissociated to approximately the same extent in isotonic solutions.

Ethylene oxide is often stated to be a strong base, because it is capable of displacing metallic radicles from their salts when dissolved in water. This reaction takes place, however, only when the hydroxide thereby produced is insoluble. The first phase of the action is the hydrolytic dissociation of the dissolved metallic salt into free acid and free basic hydroxide. The equilibrium is destroyed by the addition of ethylene oxide, which absorbs some of the acid, and causes further hydrolysis of the salt, the reaction taking place in accordance with the equation $C_2H_4(OH)Cl + M{\cdot}OH \rightleftarrows C_2H_4O + H_2O + MCl$. A certain amount of the hydroxide must be present in solution to maintain the equilibrium, and if the substance is very insoluble the required proportion is not attained and the decomposition continues until the whole of the metallic radicle is precipitated. If the salt is only slightly hydrolysed, the precipitation is very slow, as in the case of magnesium chloride; alumina, however, is rapidly thrown down, because its salts are almost completely dissociated in aqueous solution. G. T. M.

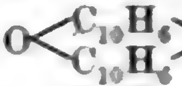
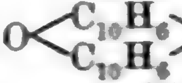
Double Compounds of the Oximes of Tetrahydropyrone Derivatives. By A. POSNIAKOFF (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 667—669).—*o-Dipropoxydiphenyltetrahydropyrone*,

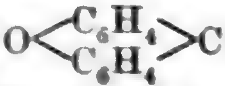
$$CO{<}\begin{matrix}CH_2{\cdot}CH(C_6H_4{\cdot}OPr)\\CH_2{\cdot}CH(C_6H_4{\cdot}OPr)\end{matrix}{>}O,$$

prepared by a method analogous to that employed by Petrenko-Kritschenko for obtaining the corresponding *o*-diethoxy-compound (see Abstr., 1899, i, 440), separates from alcohol in crystals melting at 112—113°. Its *oxime* is deposited in white crystals which melt at 170° and dissolve in alcohol but do not combine with it; with acetic acid, it yields a crystalline compound melting and decomposing at about 165°; the oxime also combines with chloroform and with ethylene glycol, giving well-formed crystals, but none of these compounds gives concordant results on analysis. Pyridine and quinoline also dissolve the oxime, but do not combine with it.

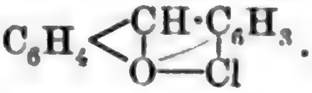
Petrenko-Kritschenko's supposition, that an increase in the size of the alkoxy-groups present in these derivatives heightens their capacity for combining with solvents, is thus seen to be erroneous (compare also Petrenko-Kritschenko, Abstr., 1900, i, 306).

The melting points of the dimethoxy-, diethoxy-, and dipropoxy-compounds are 202°, 133°, and 170° respectively. T. H. P.

New Transformation of the two Xanthhydrols into Xanthenes. By ROBERT FOSSE (*Compt. rend.*, 1901, 133, 880—882).—*Dinaphthoxanthhydrol*,  $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CH\cdot OH$, obtained by treating bromodinaphthoxanthene,  $O<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}>CHBr$, with an alcoholic solution of potassium hydroxide, crystallises in colourless needles and melts at 144°. When fused, this substance yields the corresponding *ether*, $(C_{21}H_{11}O)_2O$, a compound melting at 250°.

Dinaphthoxanthhydrol and xanthhydrol,  $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH\cdot OH$, when treated with fuming hydrochloric or hydrobromic acid, regenerate the corresponding chloro- or bromo-xanthen.

These xanthen derivatives containing a halogen behave like the salts of amines, giving rise to double salts with mercuric and platinic chlorides (compare Collie, Trans., 1900, 76, 1114). The haloid xanthen derivatives, when boiled with absolute alcohol, behave like diazonium salts, exchanging their halogen for hydrogen with formation of acetaldehyde and the corresponding halogen acid. G. T. M.

Basic Properties and Quadrivalence of Oxygen in the Xanthone Series. By ROBERT FOSSE (*Compt. rend.*, 1901, 133, 1218—1220. Compare Abstr., 1901, i, 604, 643; and this vol., i, 51).—From a solution of dinaphthoxanthone in acetic acid and platinic chloride, a *platinichloride*, $CH_2{:}(C_{10}H_6)_2{:}O,PtCl_4$, is obtained as a bright red, crystalline precipitate. The opinion is expressed that in the mono-halogenated naphthoxanthones previously described (*loc. cit.*) the oxygen atom is quadrivalent, and that the monochloro-derivative is represented by the formula  $C_6H_4<\begin{matrix}CH\cdot C_6H_3\\ | \qquad | \\ O—Cl\end{matrix}$. The fact that this compound behaves as a hypochlorite is thus accounted for.

K. J. P. O.

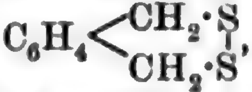
Xanthones from 2-Hydroxy-3-naphthoic Acid. Formation of Xanthones. By ERICH STROHBACH (*Ber.*, 1901, 34, 4136—4146).—*Phenyl 2-hydroxy-3-naphthoate*, $OH\cdot C_{10}H_6\cdot CO_2Ph$, prepared by heating a mixture of phenol, 2-hydroxy-3-naphthoic acid, and phosphorus oxychloride at 130°, crystallises from dilute alcohol in leaflets melting at 128—129° and boiling at 257—261° under 160 mm. pressure. The *acetyl* derivative, $OAc\cdot C_{10}H_6\cdot CO_2Ph$, obtained from the preceding compound by Liebermann's method, melts at 186·5°.

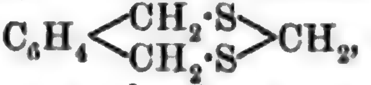
p-*Tolyl 2-hydroxy-3-naphthoate*, $OH\cdot C_{10}H_6\cdot CO_2\cdot C_6H_4Me$, crystallises in pale yellow needles, and melts at 90—90·5°; it is readily soluble in the ordinary organic solvents.

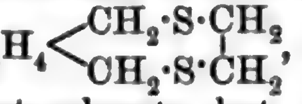
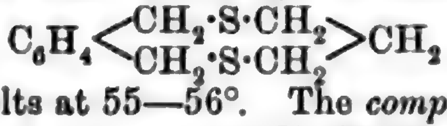
The phenyl ester, when heated at its boiling point, evolves phenol and yields γ-dinaphthoxanthone; the *p*-tolyl derivative under these conditions condenses without elimination of *p*-cresol to form 2-*methyl-γ-phenonaphthoxanthone*, a substance separating from glacial acetic acid in pale yellow crystals and melting at 158—159°.

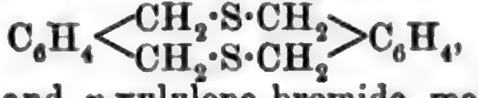
The communication also contains a discussion of syntheses in the xanthone series which is not suitable for abstraction. G. T. M.

Heterocyclic Compounds. By ARTHUR KÖTZ and OTTO SEVIN (*J. pr. Chem.*, 1901, [ii], **64**, 518—529).—A summary is given of the methods which have been employed in the preparation of ring-compounds containing carbon and sulphur.

m-*Xylylene disulphide*,  $C_6H_4{<}\begin{array}{l}CH_2\cdot S\\ \quad\ \ \vert\\ CH_2\cdot S\end{array}$, is a white, amorphous substance which melts at 115—116°. p-*Xylylene disulphide* is a white, amorphous substance, and melts at 168—169°.

o-Xylylenethiol condenses with methylene iodide to form the o-*mercaptal*,  $C_6H_4{<}\begin{array}{l}CH_2\cdot S\\ CH_2\cdot S\end{array}{>}CH_2$, which separates from chloroform in thick, transparent, odourless crystals and melts at 152—153°. The m-*mercaptal* is a white, amorphous, odourless powder, melts at 73°, and is soluble in chloroform. The p-*mercaptal* is a white, amorphous, odourless powder, and melts at 149—150°.

p-Xylylenethiol condenses with ethylene bromide to a white, amorphous *compound*,  $C_6H_4{<}\begin{array}{l}CH_2\cdot S\cdot CH_2\\ \qquad\qquad\ \vert\\ CH_2\cdot S\cdot CH_2\end{array}$, which melts at 113—114°, and is insoluble in most solvents, but dissolves readily in chloroform. The *compound*  $C_6H_4{<}\begin{array}{l}CH_2\cdot S\cdot CH_2\\ CH_2\cdot S\cdot CH_2\end{array}{>}CH_2$ is a white, amorphous compound, and melts at 55—56°. The *compound*



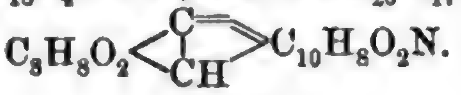
$$C_6H_4{<}\begin{array}{l}CH_2\cdot S\cdot CH_2\\ CH_2\cdot S\cdot CH_2\end{array}{>}C_6H_4,$$

from *p*-xylylenethiol and *p*-xylylene bromide, melts at 192—193° and is insoluble in all solvents; molecular weight determinations in nitrobenzene and chloroform solutions gave values corresponding with the formula $(C_{16}H_{14}S_2)_3$. T. M. L.

Gaze's "Pure Berberine." By HARRY M. GORDIN and C. G. MERRELL (*Arch. Pharm.*, 1901, **239**, 626—637).—The substance obtained by boiling acetoneberberine with chloroform and alcohol is not berberine, as Gaze supposed (Abstr., 1890, 1011), but berberine hydrochloride, $C_{20}H_{17}O_4N,HCl,2H_2O$. Berberine appears to act on chloroform as alkaline mineral bases do, converting it into hydrochloric and formic acids. Piperidine, which resembles berberine in absorbing carbon dioxide from the air, has the same action on chloroform; hydrastine, quinine, and morphine have not (for strychnine, compare Trowbridge, Abstr., 1900, i, 187). C. F. B.

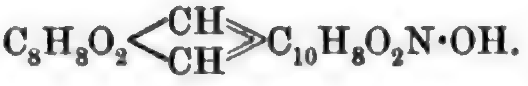
Relationship of Canadine to Berberine. By Johannes Gadamer (*Arch. Pharm.*, 1901, **239**, 648—663).—When the hydrochloride of hydroberberine, which is optically inactive, is treated with half the equivalent amount of ammonium *d*-*o*-bromocamphorsulphonate, the salt of a lævorotatory base is precipitated along with hydroberberine, whilst a dextrorotatory base remains in solution. The former melts at 132° and has $[\alpha]_D$ $-298{\cdot}2°$ in 1 per cent. chloroform solution; the second melts at 139—140°, although occasionally, when still impure, it melted at 132—133°, and has $[\alpha]_D$ $297{\cdot}4°$. A specimen of canadine melted at 132—133° and had $[\alpha]_D$ $-298{\cdot}0°$; canadine seems, however, also to have been obtained with the melting point 140°. Evidently canadine is identical with the lævorotatory base obtained from hydroberberine, and hydroberberine must be either *r*- or *dl*-canadine.

It has been assumed generally that berberine is a tertiary base. Its compound with methyl iodide, however, is not a true ammonium iodide derivative, but is rather of the same nature as the compounds with chloroform, acetone, alcohol, &c. Moreover, berberine is a strong base, very different from hydroberberine and canadine. On these grounds, the author regards berberine as a quaternary ammonium base, and modifies Perkin's formula accordingly, regarding the alkaloid as $C_{20}H_{18}O_4N{\cdot}OH$, and not $C_{20}H_{17}O_4N$.



$$C_8H_8O_2\!\left<\begin{matrix}C\\ | \\ CH\end{matrix}\right>C_{10}H_8O_2N.$$

Perkin.



$$C_8H_8O_2\!\left<\begin{matrix}CH\\ CH\end{matrix}\right>C_{10}H_8O_2N{\cdot}OH.$$

Gadamer.

C. F. B.

Hydroxycinchotine. By W. Widmar (*Monatsh.*, 1901, **22** 976—982).—When boiled with moderately dilute sulphuric acid, the so-called cinchoninesulphonic acid yields a small quantity of *β*-*iso*cinchonine and a base, $C_{19}H_{24}O_2N_2$, which the author considers to be *hydroxycinchotine* (*hydroxydihydrocinchonine*). The base melts at 268° and has $[\alpha]_D$ $+200{\cdot}79°$ at 15°, measured in an alcohol-chloroform solution.

The *sulphate*, $(C_{19}H_{24}O_2N_2)_2,H_2SO_4,8H_2O$, forms white, thick prisms which melt at 233—234°. The *hydrochloride*, $C_{19}H_{24}O_2N_2,HCl$, melts at 227—229°. The *platinichloride*, $(C_{19}H_{24}O_2N_2)_2,H_2PtCl_6$, crystallises in well-defined, rhombic plates.

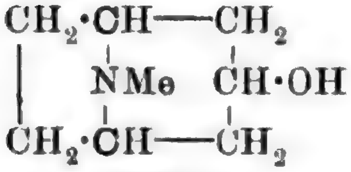
The base is quite distinct from Jungfleisch and Léger's hydroxycinchonines, and from the isomeric compound obtained by Schmid on fusing cinchotinesulphonic acid. The results agree with Skraup's suggestion (Abstr., 1901, i, 404) that the substance described as cinchoninesulphonic acid is an additive compound of cinchonine and sulphuric acid. G. Y.

Hyoscine and Atroscine. By Johannes Gadamer (*J. pr. Chem.*, 1901, [ii], **64**, 566—568).—Controversial; a reply to O. Hesse (this vol., i, 51). T. M. L.

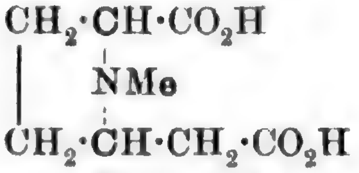
Change of Atroscine into *i*-Scopolamine. By HERMANN KUNZ-KRAUSE (*J. pr. Chem.*, 1901, [ii], **64**, 569—571).—Confirmation is given by melting point determinations of Gadamer's statement that dry atroscine passes spontaneously into *i*-scopolamine (Abstr., 1898, i, 91). T. M. L.

Ibogine. The Active Principle of a Plant of the Tabernæmontana Genus growing in the Congo. By ALBIN HALLER and EDOUARD HECKEL (*Compt. rend.*, 1901, **133**, 850—853. Compare Dybowski and Landrin, this vol., i, 114).—*Ibogine*, $C_{26}H_{32}O_2N_2$, the active principle of various species of *Iboga* (*Aboua*) growing in the Congo, is extracted from the bark of the stems and roots and also from the leaves of these plants by alcohol, the macerated material having been first digested with hot light petroleum and with chloroform; it crystallises in orthorhombic forms, melts at 152°, and has $[\alpha]_D$ −12·88°. The alkaloid has a bitter taste and is alkaline to litmus; it is insoluble in water but dissolves in the ordinary organic solvents. The salts of the alkaloid are amorphous, and the substance is not hydrolysed on boiling it with dilute sulphuric acid. Its alcoholic solutions do not reduce Fehling's solution or ammoniacal silver nitrate. The product, when derived from the stems of the plants, is accompanied by another substance melting at 206—207°. G. T. M.

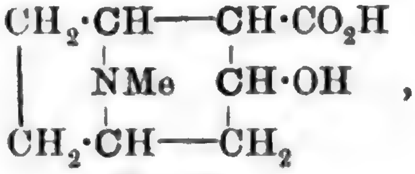
Tropic Acids and the Optical Function of the Asymmetric Carbon Atoms in Tropine and Ecgonine. By JOHANNES GADAMER (*Arch. Pharm.*, 1901, **239**, 663—671).—It is known that tropine yields an optically inactive tropic acid when oxidised, whereas both *d*- and *l*-ecgonine (these are not optical antipodes) yield an active *d*-tropic acid.



Tropine.



Tropic acid.



Ecgonine.

As even tropine from hyoscyamine is optically inactive, and as naturally occurring compounds with asymmetric carbon atoms are usually active and not mixtures of optical antipodes, it is probable that tropine is inactive by internal compensation, its two similar asymmetric carbon atoms (printed in thicker type in the formula) being respectively *d* and *l*. By oxidation to tropic acid, the symmetry of the molecule is destroyed, and the two asymmetric carbon atoms are no longer similar. The inactive tropic acid thus obtained is therefore probably susceptible of resolution into active components. The author has effected this resolution by crystallisation of the cinchonine salt from a mixture of alcohol and acetone. From the less soluble portion, l-*tropic acid* was prepared with $[\alpha]_D$ −14·8° to −15·2° in 2—6·5 per cent. aqueous solution at 20°, and melting point 243°; the ammonium salt had $[\alpha]$ +16·5° in 3 per cent. aqueous solution at 20°. From the mother liquor of the insoluble cinchonine salt d-*tropic acid* was obtained, but only in the impure state, with $[\alpha]_D$ +7·4° in 14 per cent. aqueous solution at 20°. As tropic acid from ecgonine has $[\alpha]_D$ +14·9° to +15·1° (Liebermann, Abstr., 1891, 749), it is presumably identical with *d*-tropic acid from tropine, and consequently the two left-hand asymmetric carbon atoms in ecgonine must be respectively *d*- and *l*-, as in tropine and the tropic acid obtained from it.

The author also discusses the nature of the two other asymmetric carbon atoms in ecgonine. C. F. B.

Ferrous Chloride Pyridine. By PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1901, **29**, 138—139).—Chromium chloride pyridine (Abstr., 1900, i, 559), when heated with iron, gives large, greenish, transparent crystals, which become yellowish when pulverised. The substance is probably identical with the compound, $FeCl_2,3C_5NH_5,2H_2O$, described by Reitzenstein (Abstr., 1900, i, 162), as the ratio of $Fe:Cl:C_5NH_5$ has been found to be nearly 1 : 2 : 3. J. McC.

2- and 4-Benzoylpyridines and their Derivatives. By A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 700—707).—The oxidation of 2- and 4-benzylpyridines to the corresponding benzoylpyridines is best effected by means of potassium permanganate in neutral solution, the yields obtained reaching about 90 per cent.

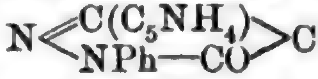
2-*Benzoylpyridine*, $COPh\cdot C_5H_4N$, obtained as a liquid boiling at 317° under 763 mm. pressure, dissolves in water, alcohol, or ether, does not solidify when cooled in ice and salt, and has the sp. gr. 1·1558 at 20°/0° and 1·1710 at 0°/0°. It has feeble basic properties, and dissolves in mineral acids, but all its salts are hydrolysed by large proportions of water with the separation of the base as an oil. The *platinichloride*, $(C_{12}H_9ON)_2,H_2PtCl_6$, crystallises from water, by which it is partially decomposed, in the form of aggregates of yellow crystals. The *picrate*, $C_{12}H_9ON,C_6H_3O_7N_3$, separates from alcohol or acetone in short prisms with rhombic bases melting at about 130° with slight decomposition. The *phenylhydrazone*, $C_{18}H_{15}N_3$, is deposited from alcohol in faintly yellow crystals melting at 136—137°. 2-Benzoylpyridine yields two isomeric *oximes*, which are formed simultaneously but can be readily separated by crystallisation, since one form is deposited in cubes melting at 150—152° whilst the other isomeride is obtained as tetrahedra melting at 165—167°. If a large excess of hydroxylamine is employed, the cubic modification is obtained in predominating proportion. The configurations of the two forms were not determined.

4-*Benzoylpyridine* crystallises from light petroleum in thin plates melting at 72° and boils at 315° under 762 mm. pressure; it is soluble in water, alcohol, or ether, and also in mineral acids, yielding salts which are readily decomposed by water. The *platinichloride* separates in needles and is completely decomposed by water; the *picrate* crystallises from alcohol in feathery aggregates, which melt and slightly decompose at 160° and are soluble in acetone. The *phenylhydrazone* separates from alcohol in faintly yellow crystals melting at 181—182°. Two *oximes* were also obtained in this case, the one obtained in the larger quantity separating from alcohol in prisms melting at 176—177°, whilst the other forms small crystals melting at 152—155°. No trace could be found of the oxime melting at 163—165, described by Freund (Abstr., 1898, i, 43) and by Fulda (Abstr., 1900, i, 53). T. H. P.

Esters of Pyridoylacetic Acids. By ADOLF PINNER [and M. DONCHI, PAUL DREXLER, and B. BAY] (*Ber.*, 1901, **34**, 4234—4253).—A detailed description of the pyridoylacetates (see Abstr., 1900, i, 409). These, when treated with hydrochloric acids, yield the ketones $C_5NH_4\cdot COMe$, which, like the ketonic acids, easily form oximes, hydrazones, and pyrazolones. The cyanohydrins of the ketones decompose when treated with hydrochloric acid, yielding carbinols,

$$C_5NH_4\cdot CHMe\cdot OH,$$

which reduce Fehling's solution in the cold.

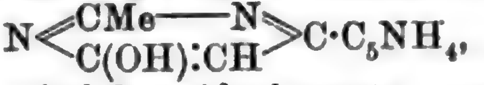
Ethyl 2-pyridoylacetate decomposes when distilled, but forms stable salts; the *sodium* derivative crystallises in needles and melts and decomposes at 234°; the *potassium* and *copper* derivatives also crystallise in needles, the *hydrochloride*, *sulphate*, and *nitrate* are unstable, but the *platinichloride* crystallises in thick, red plates and melts at 175°. The *phenylhydrazone* crystallises from methyl alcohol in long, lustrous, yellowish needles, melts at 122°, and forms a *picrate* which crystallises in yellow, felted needles melting at 197°. 3-α-*Pyridoyl*-1-*phenylpyrazolone*,  $N{<}\genfrac{}{}{0pt}{}{C(C_5NH_4)}{NPh—CO}{>}CH_2$, crystallises from benzene in small nodules and melts at 179°; the potassium derivative of ethyl 2-pyridoylacetate, when oxidised by iodine, yields *ethyl di-2-pyridoylsuccinate*, $C_2H_2(CO\cdot C_5NH_4)_2(CO_2Et)_2$, which crystallises in colourless, rhombic prisms, melts at 137°, and forms a *platinichloride* crystallising in red plates and melting and decomposing at 217°; the ester, when treated with ammonia, yields *ethyl 2-pyridoylaminocrotonate*,

$$C_5NH_4\cdot C(NH_2)\colon CH\cdot CO_2Et,$$

which crystallises from alcohol, melts at 63°, and is immediately decomposed by acids into ammonia and the acetate; the salts of the acetate react with alkyl haloids forming the alkyl esters, but these are all unstable liquids; 2-pyridyl methyl ketone forms a hygroscopic *hydrochloride* melting at 183—185°, a *platinichloride* crystallising in prisms and melting at 220°, and an amorphous *nitrate* melting and decomposing at 125°. The corresponding *carbinol* was not obtained in the pure state, as the melting point of the recrystallised product varied, probably owing to the formation of its pinacone; it forms, however, a stable *hydrochloride* melting at 205°, and *platinichloride* which crystallises, with $1\frac{1}{2}H_2O$, in yellow prisms and melts at 218° when anhydrous.

The unstable *ethyl β-2-pyridoylpropionate*, obtained either by the condensation of ethyl α-pyridinecarboxylate and ethyl propionate or by the methylation of *ethyl 2-pyridoylacetate*, forms an amorphous platinichloride melting at 175°, and when warmed with hydrochloric acid, yields 2-pyridyl ethyl ketone; the latter forms a *hydrochloride* which crystallises in small, deliquescent prisms melting at 148—150°, and a *platinichloride* which crystallises in reddish, lustrous prisms melting at 188°. The analogous 2-*pyridoylethylacetate* easily yields 2-pyridyl propyl ketone, which forms a crystalline *picrate* melting at 75°. 2-*Pyridyl phenethyl ketone*, obtained by treating the sodium salt of ethyl 2-pyridoylacetate with benzyl chloride, is an unstable oil and forms a crystalline *platinichloride* melting at 188° and a *picrate* melting at 129°.

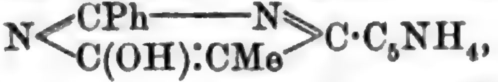
The pyridoylacetates easily condense with amidines forming hydroxypyrimidines. 4-α-*Pyridyl*-6-*hydroxy*-2-*methylpyrimidine*,



$$N{<}^{CMe\text{---}N}_{C(OH):CH}{>}C\cdot C_5NH_4,$$

from acetamidine and ethyl 2-pyridoylacetate, crystallises from alcohol in needles, melts at 270°, and forms an amorphous, insoluble silver salt. 4-α-*Pyridyl*-6-*hydroxy*-2-*phenylpyrimidine* crystallises in needles, melts at 268°, is soluble in alkalis and mineral acids, and forms a *platinichloride* which crystallises in needles melting at 268°; the *ethyl* ether crystallises in prisms, melts at 120°, and forms a *platinichloride* melting at 205°; the *acetyl* derivative crystallises in needles melting at 150°, and, when heated, yields the *anhydride* of the hydroxypyrimidine, $(C_{15}H_{10}N_3)_2O$, which crystallises from alcohol in needles, and melts at 208°. This reaction seems to be a general one for the acetyl derivatives of hydroxypyrimidines.

4-α-*Pyridyl*-6-*hydroxy*-2-*phenyl*-5-*methylpyrimidine*,



$$N{<}^{CPh\text{---}N}_{C(OH):CMe}{>}C\cdot C_5NH_4,$$

from ethyl β-2-pyridoylpropionate and benzamidine, crystallises from alcohol in prisms melting at 230°; it forms an amorphous *platinichloride* melting at 238°, and an *acetyl* derivative which crystallises in prisms, melts at 104°, and yields an anhydride when heated.

Ethyl 3-pyridoylacetate forms a *potassium* salt which crystallises from acetone in needles, an amorphous *copper* salt, an amorphous *silver* salt, and a *platinichloride*.

Ethyl 4-pyridinecarboxylate is a colourless liquid which boils at 110° under 15 mm., and at 219—220° under atmospheric pressure, and has a sp. gr. 1·0091 at 15°; its *hydrochloride* crystallises in hygroscopic, lustrous needles and melts at 165°; its *platinichloride* is an amorphous, orange-yellow precipitate.

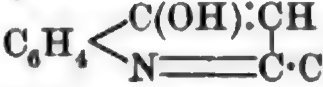
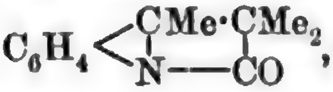
Ethyl 4-pyridoylacetate crystallises in thick bundles of prisms melting at 54°; the *sodium* and *potassium* derivatives crystallise in needles; the *copper* derivative is crystalline, and melts at 183—184°, and the *silver* derivative is amorphous; the *platinichloride* crystallises in orange-red leaflets, and melts at 156°. The *phenylhydrazone* crystallises in small needles, and, when heated, is converted into 3-γ-*pyridyl*-1-*phenylpyrazolone*, which crystallises from methyl alcohol, and melts at 215°; *ethyl di-4-pyridoylsuccinate* crystallises in small needles melting at 197°. 4-*Pyridyl methyl ketone* is an oil which boils at 212—214° and is easily soluble in alcohol, ether, or acids; its *hydrochloride* is deliquescent; the *platinichloride* crystallises in lustrous leaflets melting at 205°, the *mercurichloride* in needles melting at 183—184°, the *picrate* in leaflets melting at 130°, the *phenylhydrazone* in yellow needles melting at 150°, and the *oxime* in lustrous needles melting at 142°. When treated with methyl iodide, the sodium derivative of ethyl 4-pyridoylacetate yields the *methiodide* of 4-pyridyl ethyl ketone, which, when treated with silver chloride, is converted into the *methochloride*; the latter crystallises in very deliquescent needles, and forms a *platinichloride* which crystallises in needles, melting and decomposing at 205°, and an *aurichloride* which crystallises in yellow, lustrous plates and melts at 163—164°. 4-*Pyridyl propyl ketone* is an oil boiling at 229—231°, and forms a *picrate* which crystallises in long, yellow needles melting at 96°.

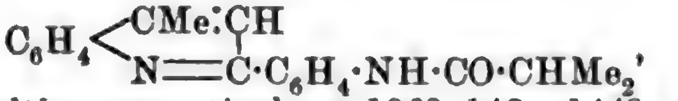
4-*Pyridyl butyl ketone* boils at 239—240°, and its *picrate* crystallises in needles melting at 101°.

The *ethyl* ester of 2-methylpyridine-6-carboxylic acid (Abstr., 1900, i, 409) boils at 133° under 35 mm. pressure, and when treated with ethyl acetate and sodium ethoxide yields *sodium* 2-*methyl*-6-*pyridoylacetate* which crystallises in yellow nodules from alcohol; the *acid* is an oil which cannot be distilled, the *potassium* salt crystallises from acetone in long needles. 2-*Methyl*-6-*pyridyl methyl ketone* is a colourless oil boiling at 198—200°; it forms a *platinichloride* melting at 162°.

R. H. P.

Ethyl Dihydroxycinchomeronate. By SIEGFRIED RUHEMANN (*Ber.*, 1901, **34**, 4165).—A claim for priority (compare Trans., 1900, **67**, 250, and Errera and Perciabosco, this vol., i, 116). W. A. D.

Synthesis of 2- and 4-Hydroxyquinolines. By RUDOLF CAMPS (*Arch. Pharm.*, 1901, **239**, 591—610. Compare Abstr., 1900, i, 115, 310).—When *o*-*iso*butyrylaminoacetophenone (Bischler, Abstr., 1893, i, 531), $CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot CHMe_2$, is boiled with a dilute solution of sodium hydroxide in alcohol and water, 4-hydroxy-2-*iso*propylquinoline,  $C_6H_4<\begin{array}{l}C(OH):CH\\ N=\!=C\cdot CHMe_2\end{array}$, 3 : 3 : 4-trimethyl-2-quinolone,  $C_6H_4<\begin{array}{l}CMe\cdot CMe_2\\ N-\!-CO\end{array}$, and *iso*butyryl-*o*-flavaniline,



$$C_6H_4<\begin{array}{l}CMe:CH\\ N=\!=C\cdot C_6H_4\cdot NH\cdot CO\cdot CHMe_2\end{array},$$

are obtained, melting respectively at 196°, 143—144°, and 117°.

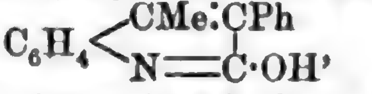
o-Benzoylaminoacetophenone (Bischler, *loc. cit.*), under similar circumstances, yields 4-hydroxy-2-phenylquinoline (Knorr, Abstr., 1888, 1113), together with a little *benzoyl-o-flavaniline*, which melts at 150°. That Bischler could not effect a similar condensation was due to the fact that the alcohol he employed was free from water.

Aminoacetophenone condenses with ethyl chloroformate, in anhydrous ethereal solution, to form *ethyl o-acetylphenylcarbamate*,

$$CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO_2Et.$$

This melts at 91° and yields a little 2 : 4-dihydroxyquinoline (Friedländer and Weinberg, Abstr., 1883, 351) when it is boiled with dilute aqueous alcoholic sodium hydroxide, although for the most part it is decomposed into carbon dioxide and aminoacetophenone.

With phenylacetyl chloride in anhydrous ethereal solution, aminoacetophenone condenses to form *phenylacetyl-o-aminoacetophenone*, $CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Ph$. This melts at 79—80°; when boiled with dilute aqueous alcoholic sodium hydroxide, it is converted almost quantitatively into 2-*hydroxy*-3-*phenyl*-4-*methylquinoline*,



$$C_6H_4<\begin{array}{l}CMe:CPh\\ N=\!=C\cdot OH\end{array},$$

which melts at 275°, no isomeric 4-hydroxy-2-benzylquinoline being formed.

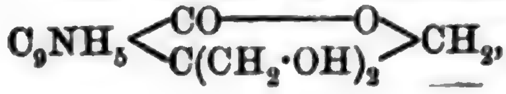
The other results described in the paper have been published already (Abstr., 1901, i, 751). C. F. B.

Condensations of Formaldehyde with Pyridine and Quinoline Derivatives. By WILHELM KOENIGS (*Ber.*, 1901, **34**, 4322—4326. Compare Abstr., 1899, i, 74, 389; 1900, i, 189).—The number of hydrogen atoms in a 2- or 4-derivative of pyridine or quinoline which can be replaced by methylol, $\cdot CH_2\cdot OH$, groups by the action of formaldehyde is always lessened by one when the 3- or 5-position contains as a substituent an alkyl group or a benzene nucleus. The same generalisation holds when both 3- and 5-positions are substituted. If, however, the 3- or 5-position is occupied by a carboxyl group, the introduction of methylol is facilitated rather than retarded.

Neither 2-methylpyridine nor 2-methylquinoline forms condensation products with paraldehyde, chloral, or benzaldehyde. J. J. S.

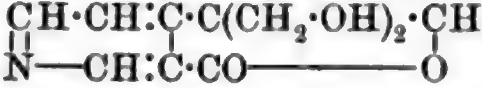
Condensation of Formaldehyde with 2-Ethylquinoline and with 3-Methyl-2-ethylquinoline. By WILHELM KOENIGS and EDUARD BISCHKOPF (*Ber.*, 1901, **34**, 4327—4330. Compare preceding abstract).—*2-α-Dimethylolethylquinoline*, $C_9NH_6\cdot CMe(CH_2\cdot OH)_2$, is formed when 2-ethylquinoline is heated with excess of a solution of formaldehyde under pressure for 48 hours; it crystallises from petroleum in colourless needles melting at 95—96°; the *hydrochloride* crystallises in colourless needles melting at 178—179°; the *aurichloride* forms pale yellow granules, and the *mercurichloride* greyish-white flakes. *2-α-Methylolethyl-3-methylquinoline*, $C_{15}H_{15}ON$, prepared from 3-methyl-2-ethylquinoline and formaldehyde, is a crystalline solid melting at 87—88°; the *platinichloride* crystallises in reddish-yellow needles melting and decomposing at 200—205°; the *mercurichloride* forms white crystals, the *aurichloride* pale yellow needles, and the *cadmioiodide* pale yellow crystals melting and decomposing at 157—160°. Attempts to prepare 2-α-dimethylolethyl-3-methylquinoline failed. 3-Methylquinoline does not condense with aldehydes, and thus resembles β-picoline. K. J. P. O.

Condensation of β-Methylquinaldine [2:3-Dimethylquinoline] and of 2-Methylquinoline-3-carboxylic Acid with Formaldehyde. By WILHELM KOENIGS and FERDINAND STOCKHAUSEN (*Ber.*, 1901, **34**, 4330—4336. Compare preceding abstracts).—*Dimethylol-β-methylquinaldine* [2-dimethylolmethyl-3-methylquinoline], $C_9NH_5Me\cdot CH(CH_2\cdot OH)$, is prepared by heating 2:3-dimethylquinoline with formaldehyde under pressure at 100°, and crystallises with H_2O in long needles melting at 85—86°; when anhydrous, it melts at 106—108°. The *platinichloride* crystallises in small, yellow needles melting and decomposing at 193°; the *hydrochloride* forms needles melting and decomposing at 200—201°; the *aurichloride*, yellow needles melting at 145°; the *cadmiochloride* crystallises in white needles melting and decomposing at 207—209°, the *mercurichloride* in white needles melting at 136°; the *picrate* crystallises in long, yellow, silky needles melting at 170°. On oxidation with nitric acid, the base yields 3-methylquinoline-2-carboxylic acid (m. p. 144°).

The *lactone* of 2-trimethylolmethylquinoline-3-carboxylic acid,  $C_9NH_5\left<\begin{matrix}CO\text{———}O\\ C(CH_2\cdot OH)_2\end{matrix}\right>CH_2$, is formed when 2-methylquinoline-3-

carboxylic acid is heated at 100° for many hours with great excess of formaldehyde under pressure, and crystallises from water with H_2O in white needles melting at 167—168°; the *hydrochloride* crystallises in long, white needles melting and decomposing at 189—191°; the *platinichloride* crystallises, with $2H_2O$, in red needles, plates, or leaflets, which darken at 180° and finally melt and decompose at 216—217°; the *aurichloride* crystallises in long, thin, golden-yellow needles, melting and decomposing at 209—210°; the *picrate* forms tufts of yellow, lustrous needles, melting and decomposing at 142—143°. When oxidised with nitric acid, acridinic acid (Graebe and Caro, Abstr., 1880, 398) is obtained. The lactone is insoluble in sodium carbonate, but immediately dissolves in sodium or barium hydroxide; carbon dioxide reprecipitates the lactone from these solutions. K. J. P. O.

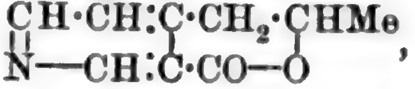
Condensation Products of Homonicotinic Acid [4-Methylpyridinecarboxylic Acid] with Formaldehyde and Acetaldehyde. By Wilhelm Koenigs (*Ber.*, 1901, **34**, 4336—4342. Compare preceding abstracts).—When homonicotinic acid is heated with formaldehyde solution under pressure at 100°, the *lactone* of 4-trimethylolmethylpyridine-3-carboxylic acid,



$$\begin{array}{l} CH\cdot CH{:}C\cdot C(CH_2\cdot OH)_2\cdot CH_2 \\ N{-}CH{:}C\cdot CO{-}{-}{-}{-}O \end{array},$$

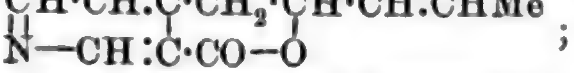
is formed; it crystallises from ethyl acetate in colourless needles melting at 148°; the *hydrochloride* is very soluble in water; the *aurichloride* crystallises in yellow, flattened needles or plates, the *platinichloride* in orange-red, four-sided plates melting and decomposing at 230°; the *picrate* crystallises in pale yellow needles or scales, which melt and decompose at 204°. A *monoacetyl* derivative is obtained by boiling the crude lactone with excess of acetic anhydride, and crystallises in colourless prisms which melt at 153—154°, and volatilise undecomposed. When heated with aqueous sodium hydroxide, an amorphous sodium salt is formed. Oxidising agents, especially nitric acid, convert the lactone into cinchomeronic acid.

When acetaldehyde (or paraldehyde) and homonicotinic acid are heated at 140—150° under pressure, two substances are formed which can be separated by fractional crystallisation of their picrates from water. From the more soluble picrate (m. p. 143°), the *platinichloride* of the lactone of ethylol-homonicotinic acid,



$$\begin{array}{l} CH\cdot CH{:}C\cdot CH_2\cdot CHMe \\ N{-}CH{:}C\cdot CO{-}O \end{array},$$

is obtained in reddish-yellow crystals, which darken at 240° but do not melt at 278°. From the less soluble picrate (m. p. 186°), a *platinichloride*, $(C_{11}H_{11}O_2N)_2,H_2PtCl_6$, is obtained in yellowish-red crystals melting and decomposing at 238°. The author believes the base to be the lactone of crotonylol-homonicotinic acid,



$$\begin{array}{l} CH\cdot CH{:}C\cdot CH_2\cdot CH\cdot CH{:}CHMe \\ N{-}CH{:}C\cdot CO{-}O \end{array};$$

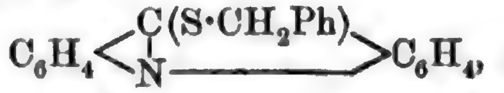
the base exhibits a blue fluorescence in solution in ethyl acetate; with cadmium chloride, the hydrochloride of the base gives a double *salt* crystallising in yellow needles, melting and decomposing at 230—231°.

K. J. P. O.

Acridine. II. By Albert Edinger and W. Arnold (*J. pr. Chem.*, 1901, [ii], **64**, 471—492. Compare Abstr., 1901, i, 753).—When heated with phosphorus pentachloride and phosphorus oxychloride at 120—130°, 5-thioacridone yields 5-chloroacridine (m. p. 119°). With red phosphorus and bromine, 5-*bromoacridine*, $C_{13}H_8NBr$, is mainly obtained; it crystallises in brownish-yellow needles melting at 116°, and in the presence of acids is very readily converted into acridone; the *platinichloride* forms small, brown, quadratic crystals; the *picrate* crystallises in small, yellow needles melting at 212—213°; the *hydrochloride* forms needles decomposing at 238°, and the *sulphate* yellow needles decomposing at 170°.

5-*Iodoacridine*, $C_{13}H_8NI$, cannot be obtained by the action of phosphorus and iodine on thioacridone, but is prepared by the action of sodium iodide on 5-bromoacridine in the presence of alcohol; it crystallises in brownish-yellow needles melting at 169°; the *sulphate* crystallises in yellow needles; the *platinichloride* crystallises in brownish-yellow needles, and the *picrate* in lemon-yellow needles melting at 204°.

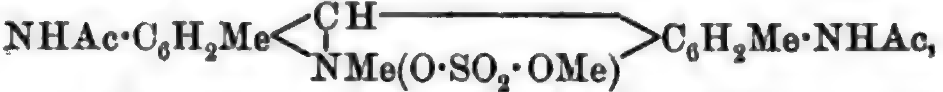
5-*Benzoylthioacridol*, $C_{13}H_8NBzS$, obtained by benzoylating thioacridone by the Schotten-Baumann method, crystallises in yellowish-green leaflets melting at 209°; the *picrate* crystallises in yellowish-green needles melting at 190°.

5-*Benzylthioacridol*,  $C_6H_4\left\langle\begin{matrix}C(S\cdot CH_2Ph)\\ |\\ N\end{matrix}\right\rangle C_6H_4$, prepared by the action of sodium ethoxide on a mixture of benzyl chloride and thioacridol dissolved in alcohol, crystallises in large, greenish-yellow needles melting at 109°; the *hydrochloride* and *nitrate* both crystallise in yellow leaflets, the former decomposing at 140—141°, the latter at 106—107°; the *platinichloride* is a brownish-yellow solid; the *picrate* crystallises in yellowish-brown, lustrous needles melting at 189—190°, whilst the *sulphate* forms yellowish-brown crystals melting and decomposing at 179—180°.

5-*Methylthioacridol*, $C_{13}H_8N\cdot SMe$, prepared by treating thioacridol and methyl iodide with sodium ethoxide in alcoholic solution, crystallises in greenish-yellow needles melting at 113—114°; the *hydrochloride* forms yellow needles melting at 198°; the *sulphate* melts at 156—157°; the *nitrate* melts and decomposes at 117—118°; the *platinichloride* is an ochre-yellow, crystalline powder, and the *picrate* forms lustrous needles melting at 205°. Alcoholic hydrochloric acid converts it into acridone and methylmercaptan. When thioacridol and methyl iodide are heated under pressure at 75—80°, the methyl ether just mentioned is formed; at 150°, a substance containing no sulphur, but much iodine, is obtained, which, with sodium carbonate, yields mainly acridone; at 250°, acridine hydriodide and iodine are produced.

A *tetranitroacridone*, $C_{13}H_4ON(NO_2)_4$, is formed when thioacridol is heated with concentrated nitric acid under pressure; it forms insoluble lemon-yellow crystals melting above 350°, and dissolves in alkalis with a cherry-red coloration. K. J. P. O.

Diaminoacridinium Compounds. By FRITZ ULLMANN and A. MARIĆ (*Ber.*, 1901, **34**, 4307—4316. Compare Abstr., 1900, i, 689).—2 : 8-Diamino-3 : 7-dimethylacridine (D.R.-P. 52324) crystallises from aniline in yellow needles, dissolves in concentrated sulphuric acid to a yellowish-green solution with a blue-green fluorescence, but is not readily soluble in organic solvents. The hydrochloride, $C_{15}H_{16}N_3Cl$, forms a microcrystalline, red powder and is only sparingly soluble in alcohol; the platinichloride is an insoluble, orange powder, and the *diacetyl* derivative crystallises from aniline in yellow needles. When dissolved in nitrobenzene and treated with methyl sulphate, the diacetyl derivative is converted into 2 : 8-*diacetylamino*-3 : 7 : 10-*trimethylacridinium methosulphate*,



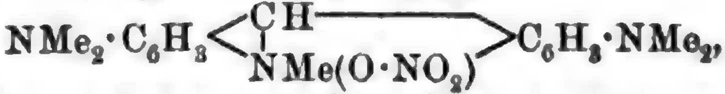
$$NHAc\cdot C_6H_2Me{<}\begin{matrix}CH\text{———————}\\ |\\ NMe(O\cdot SO_2\cdot OMe)\end{matrix}{>}C_6H_2Me\cdot NHAc,$$

in the form of a reddish-yellow, crystalline precipitate readily soluble in water and also in concentrated sulphuric acid. The *chloride*, $C_{20}H_{22}O_2N_3Cl$, crystallises from alcohol, in which it is only sparingly soluble, in small, yellow needles. The *nitrate* is an orange-yellow, crystalline powder, and the *dichromate*, $(C_{20}H_{22}O_2N_3)_2Cr_2O_7$, separates from acetic acid in yellow crystals. Most of the salts are decomposed by ammonia, yielding a pale-coloured, crystalline substance insoluble in the usual solvents.

2 : 8-*Diamino*-3 : 7 : 10-*trimethylacridinium chloride*, obtained from the acetyl derivative by the action of hydrochloric acid, or from 2 : 8-diamino-3 : 7-dimethylacridine by transformation into the methosulphate and then into the chloride, crystallises in large, red needles which are readily soluble in water, yielding an orange-coloured solution with green fluorescence. The *nitrate* crystallises in red needles, sparingly soluble in alcohol, and the *dichromate* is an orange-red powder, insoluble in alcohol.

2-Nitro-4 : 4 -tetramethyldiaminodiphenylmethane (D.R.-P. 79250) crystallises in brick-red needles melting at 95° and readily soluble in most organic solvents. On reduction with stannous chloride, it yields the 2-*amino*-derivative, which crystallises from a mixture of ether and light petroleum in pale rose-coloured plates melting at 96°. Dinitrotetramethyldiaminodiphenylmethane (Pinnow, Abstr., 1901, i, 98) melts at 195° (corr.), not 191·5°.

Tetramethyldiaminoacridine (Biehringer, Abstr., 1897, i, 73) is readily alkylated by the action of methyl sulphate in toluene solution, and when the product is treated with nitric acid, it yields 2 : 8-*tetramethyldiamino*-10-*methylacridinium nitrate*,



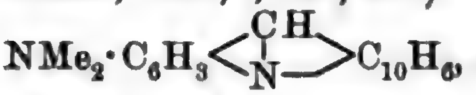
$$NMe_2\cdot C_6H_3{<}\begin{matrix}CH\text{—————}\\ |\\ NMe(O\cdot NO_2)\end{matrix}{>}C_6H_3\cdot NMe_2,$$

in the form of long, dark-red needles with a steely lustre. It dissolves in concentrated sulphuric acid, but is practically insoluble in alcohol.

All these acridinium compounds dye tannined cotton with great readiness; the colours obtained are fast to alkalis, and vary from pure yellow to orange-red.

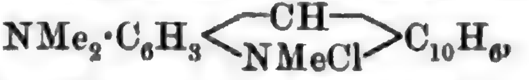
When the acridine derivatives are alkylated with halogen alkyls, they yield, even in neutral solutions, alkylated amino-derivatives and not acridinium compounds.

The dye known as patent phosphin (D.R.-P. 79703) contains no acridinium salt, but is an alkylated aminoacridine. J. J. S.

3'-Dimethylamino-[Pheno]1 : 2-naphthacridine. By Fritz Ullmann and A. Marić (*Ber.*, 1901, 34, 4317—4322. Compare Abstr., 1900, i, 360, 361).—2-*Dimethylaminopheno*-1 : 2-*naphthacridine*,  $NMe_2\cdot C_6H_3<\substack{CH\\ \mid \\ N}>C_{10}H_6$, or its leuco-derivative may be obtained by the action of β-naphthol on tetramethyltetra-aminodiphenylmethane or on the anhydroformaldehyde derivative of *m*-aminodimethylaniline, also by the action of dihydroxydinaphthylmethane on *m*-aminodimethylaniline and the action of β-naphthol on *m*-aminodimethylaniline and paraformaldehyde; the yields are good. It crystallises from a mixture of benzene and light petroleum in stellate groups of large, yellowish-red needles or in thick, quadratic plates melting at 185·5°, and dissolves in concentrated sulphuric acid and in alcohol, yielding fluorescent solutions. The *hydrochloride* forms dark-brown needles soluble in water or alcohol; the *nitrate* forms red needles sparingly soluble in water; the *dichromate* is insoluble in water, and the *picrate* crystallises in red plates insoluble in alcohol, ether, or benzene.

The *leuco*-compound, $C_{19}H_{18}N_2$, crystallises from benzene in plates melting at 202—207° and insoluble in alcohol or ether.

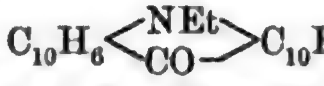
2-*Dimethylamino*-12-*methylpheno*-1 : 2-*naphthacridinium chloride*,



$$NMe_2\cdot C_6H_3<\substack{CH\\ NMeCl}>C_{10}H_6,$$

crystallises in red needles, soluble in water or alcohol to fluorescent solutions which do not change on the addition of ammonium or sodium hydroxide solutions. The *dichromate* is a red, crystalline powder insoluble in alcohol, but readily soluble in acetic acid. J. J. S.

Naphthacridones and Naphthacridines. By Erich Strohbach (*Ber.*, 1901, 34, 4146—4158. Compare Möhlau, Abstr., 1896, i, 242).—Naphthacridone is produced by heating 2-hydroxy-3-naphthoic acid with β-naphthylamine at 260—280° for 10—12 hours; it is accompanied by smaller quantities of $\beta\beta$-dinaphthylamine, 2-*hydroxy*-3-*naphtho*-β-*naphthalide*, $OH\cdot C_{10}H_6\cdot CO\cdot NH\cdot C_{10}H_7$, and traces of β-*naphthylamino*-3-*naphthoic acid*, $C_{10}H_7\cdot NH\cdot C_{10}H_6\cdot CO_2H$. When the heating is carried out in the presence of phosphorus oxychloride, the yield of the bye-products is increased. 2-Hydroxy-3-naphtho-β-naphthalide is more conveniently prepared by heating a mixture of methyl 2-hydroxy-3-naphthoate and β-naphthylamine with phosphorus oxychloride at 180—200°; it crystallises from pyridine or water in lustrous, yellowish-white leaflets and melts at 243—244°. β-Naphthylamino-3-naphthoic acid crystallises from alcohol or water in yellow needles and melts at 222—225°.

14-*Ethyl*-$\beta_1\beta_2a_1'\beta_1'$-*naphthacridone*,  $C_{10}H_6<\substack{NEt\\ CO}>C_{10}H_6$, obtained by heating the potassium derivative of $\beta_1\beta_2a_1'\beta_1'$-naphthacridone with excess of ethyl iodide at 130—150°, crystallises from acetone in lustrous, yellow needles melting at 204·5—205°. The ethyl compound dissolves in the ordinary organic solvents, its solutions having a green fluorescence. The solution of the substance in concentrated sulphuric acid has a reddish-orange colour, and develops a yellowish-green fluorescence on warming.

The unsymmetrical constitution is given to naphthacridone and its ethyl derivative, in view of the fact that it is the α-hydrogen atom contiguous to the β-amino-group which is displaced in condensations with β-naphthylamine (compare Lellmann and Schmidt, Abstr., 1888, 289, and Morgan, Trans., 1900, **77**, 814).

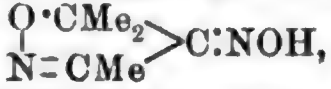
14-*Iodo-$\beta_1\beta_2\alpha_1'\beta_1'$-naphthacridine hydriodide*, $C_{10}H_6<\begin{smallmatrix}NHI\\|\\CI\end{smallmatrix}>C_{10}H_6$, results from the action of hydriodic acid of sp. gr. 1·70 on $\beta_1\beta_2\alpha_1'\beta_1'$-naphthacridone at 160—180°; it is a reddish-orange, crystalline substance darkening on exposure to light, and decomposing at 180—190°. When heated with acetone or alcohol, it reverts to naphthacridone.

$\beta_1\beta_2\alpha_1'\beta_1'$-Naphthacridine, $C_{10}H_6<\begin{smallmatrix}N\\|\\CH\end{smallmatrix}>C_{10}H_6$, produced by heating a mixture of the corresponding acridone and zinc dust in a stream of hydrogen, dissolves in pyridine and less readily in the other organic solvents; it is, however, insoluble in water. The base melts at 205·5—206°; its solutions in all solvents except concentrated sulphuric acid have a yellowish-green fluorescence.

The preceding base is termed by the author "β-naphthacridine," whilst Reed's isomeride melting at 216° (Abstr., 1886, 1037) is indicated by the index leter "α-." G. T. M.

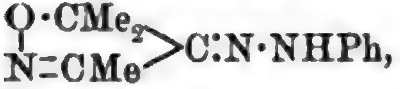
Action of Nitrous and Nitric Acids on Mesityloxideoxime. By Carl D. Harries (*Annalen*, 1901, **319**, 230—256).—Mesitylnitrimine, the product of the action of nitrous acid on the stereoisomeric mesityloxideoximes (compare Abstr., 1898, i, 400, 568; 1899, i, 566), when reduced with zinc dust and water, yields trimethyldihydropyrazoline boiling at 63—64° under 23 mm. pressure (compare Curtius and Wirsing, Abstr., 1894, i, 248). This base is also obtained by reducing the hydrogen chloride compound of the nitrimine; the nitrimine may have one or other of the following formulæ, $CH<\begin{smallmatrix}CMe\cdot N\\|\\CMe_2N\end{smallmatrix}>O$ or $CMe_2\!:\!CH\cdot CMe\!:\!N<\begin{smallmatrix}O\\|\\N\end{smallmatrix}$.

isoMesitylnitrimine (*ketotrimethyldihydroisooxazoleoxime*),

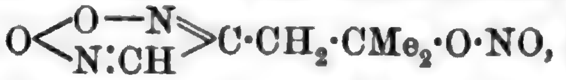


$$\begin{smallmatrix}O\cdot CMe_2\\|\\N=CMe\end{smallmatrix}>C\!:\!NOH,$$

produced by heating mesitylnitrimine with water at 120°, crystallises from chloroform in white leaflets and melts at 156—157°; it has the properties of an oxime, forms a sodium derivative, does not reduce Fehling's solution until after hydrolysis with dilute sulphuric acid, and is not affected by bromine or by zinc dust and water. Its *acetyl* derivative crystallises from light petroleum or alcohol, and melts at 68—69°.

Ketotrimethyldihydroisooxazole, $\begin{smallmatrix}O\cdot CMe_2\\|\\N=CMe\end{smallmatrix}>CO$, obtained by mixing the oxime with cold concentrated nitric acid and heating the oily product, $C_6H_9O_5N_3$, either by itself or with acetic anhydride, is a colourless, refractive oil boiling at 50—51° under 16 mm., and at 151° at the ordinary, pressure; it has a pleasant odour, and a sp. gr. 1·020 at 27°. On treatment with hydroxylamine, it regenerates *iso*mesitylnitrimine and with phenylhydrazine, the *phenylhydrazone*,  $\begin{matrix}O\cdot CMe_2\\ | \\ N{:}CMe\end{matrix}\!\!>C{:}N\cdot NHPh$, is obtained, which crystallises from alcohol or light petroleum in yellow needles melting at 140—141°.

*iso*Mesitylnitrimine, when boiled with dilute acids, is completely broken down, and nothing but a small amount of acetoxime is obtained.

Mesitylglyoximeperoxide nitrite,  $O\!<\!\begin{matrix}O—N\\ N{:}CH\end{matrix}\!>\!C\cdot CH_2\cdot CMe_2\cdot O\cdot NO$, produced by gently warming mesityloxideoxime in dilute nitric acid of sp. gr. 1·1, crystallises from methyl alcohol, acetone, glacial acetic acid, or acetic anhydride in golden-yellow leaflets or needles, and melts at 128—129°.

a-Nitromesityl-β-anil, $NO_2\cdot CH_2\cdot C(NPh)\cdot CH{:}CMe_2$, prepared by adding aniline to the preceding nitrite suspended in dry ether, crystallises from the ordinary organic solvents in yellow leaflets melting at 84—85°; it yields a-nitromesityloxide, $CMe_2{:}CH\cdot CO\cdot CH_2\cdot NO_2$, and aniline on hydrolysis with dilute mineral acids, this product being a yellow oil boiling at 95—96° under 23 mm. pressure and having a sp. gr. 1·212 at 27·3°. The nitro-group in this compound is attached to a primary carbon atom, the substance giving a well-defined sodium derivative. The nitro-compound decolorises bromine, and when treated with semicarbazide and aniline gives rise to the semicarbazone and anil derivatives of nitroacetone respectively; the former of these crystallises in needles melting at 163—164°, and the latter, which is also obtained by the action of aniline on mesitylglyoximeperoxide nitrite in glacial acetic acid, crystallises from alcohol or light petroleum in amber-coloured needles or prisms sintering at 80° and melting at 87°. The anil derivative is quantitatively hydrolysed into nitroacetone by heating with 25 per cent. sulphuric acid.

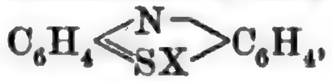
The foregoing reactions constitute a ready method of preparing nitroacetone (compare Lucas, Abstr., 1900, i, 82), 100 grams of mesityloxide furnishing 35 grams of the product.

Nitroacetone boils at 103—104° under 24 mm., and at 185—190° under the ordinary, pressure. When distilled in large quantities, it decomposes at 165° into acetic acid and a substance having an odour of prussic acid, probably cyanic acid.

The *sodium* derivative, $COMe\cdot CH{:}NO_2Na$, separates in colourless crystals, and the *silver* derivative in yellow needles. The nitro-compound neither reduces ammoniacal silver nitrate nor forms an oxide with nitrous acid; it yields acetylmethylnitrolic acid (compare Behrend and Tryller, Abstr., 1895, i, 201).

a-Nitro-γ-benzylideneacetone, $CHPh{:}CH\cdot CO\cdot CH_2\cdot NO_2$, produced by condensing nitroacetone with benzaldehyde in a 5 per cent. solution of sodium hydroxide, crystallises from alcohol in yellow plates, sinters at 83°, and melts at 87—88°. G. T. M.

Azothionium Compounds. By FRIEDRICH KEHRMANN (*Ber.*, 1901, **34**, 4170—4174).—Azothionium salts of the type

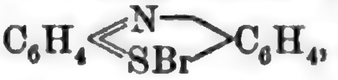


$$C_6H_4{<}\genfrac{}{}{0pt}{}{N}{SX}{>}C_6H_4,$$

analogous to the azoxonium salts (compare Abstr., 1900, i, 61; 1901, i, 484; Werner, Abstr., 1901, i, 50) are obtained by oxidising thiodiphenylamine derivatives with acid oxidising agents.

[With V. VESELY.]—*Phenazothionium ferrochloride*,

$$(C_{12}H_8NSCl)_2,FeCl_2,$$

obtained by adding a cold alcoholic solution of thiodiphenylamine to ice-cold alcoholic ferric chloride, forms brownish-green crystals. *Phenazothionium bromide*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{SBr}{>}C_6H_4$, obtained by mixing cold alcoholic solutions of thiodiphenylamine and of bromine, is a coarsely crystalline, olive-green powder. *Phenazothionium picrate* is a greyish-green, sandy, crystalline powder. W. A. D.

A New Reaction of Semicarbazones. By WALTHER BORSCHE (*Ber.*, 1901, **34**, 4297—4302. Compare Kipping, Proc., 1900, 63; Young, *ibid.*, 73).—When salicylsemicarbazone is heated at 250—300°, it yields *o*-hydroxybenzylideneazine; when boiled with aniline for some time, the products are the same azine and *s*-diphenylcarbamide, or when the boiling is continued for only a short time, a third product, phenyl-*o*-hydroxybenzylidenesemicarbazone (Curtius and Hofmann, Abstr., 1896, i, 647), is also formed.

Acetophenonesemicarbazone crystallises in colourless plates melting and decomposing at 198—199°; when boiled with aniline, it yields *acetophenonephenylcarbamic acid hydrazone* melting at 187—188°. Acetophenonesemicarbazone and *o*-toluidine yield di-*o*-tolylcarbamide and *acetophenone-o-tolylcarbamic acid hydrazone*,

$$CMePh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me.$$

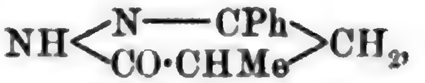
The latter crystallises from alcohol in long, colourless needles, melts at 211—212°, and is not readily converted into the corresponding azine. Acetonesemicarbazone and β-naphthylamine yield *acetone-β-naphthylcarbamic acid hydrazone* in the form of pale red needles melting at 192—193° and di-β-naphthylcarbamide. The reaction is best carried out in the presence of dimethylaniline.

Tertiary bases do not react with semicarbazones in the same manner as aniline. J. J. S.

Pyridazines. By ALFRED OPPENHEIM (*Ber.*, 1901, **34**, 4227—4234. Compare Abstr., 1899, i, 390).—Disubstituted pyridazines have been synthesised by the action of hydrazine on γ-ketonic acids of the formula $X{\cdot}CO{\cdot}CH_2{\cdot}CHR{\cdot}CO_2H$.

Benzoyldimethylmalonic acid, $CH_2Bz{\cdot}CMe(CO_2H)_2$, obtained when the sodium compound of ethyl *iso*succinate suspended in ether is treated with bromoacetophenone, is a yellow, crystalline substance which melts at 145° with the evolution of carbon dioxide, yielding an acid which is identical with the β-benzoyl-α-methylpropionic acid obtained by Klobb (Abstr., 1900, i, 498) by the condensation of pyrotartaric anhydride with benzene.

β-Benzoyl-α-methylpropionic acid condenses with hydrazine, forming

3-phenyl-5-methylpyridazinone,  $\mathrm{NH}<\begin{matrix}\mathrm{N—CPh}\\ \mathrm{CO\cdot CHMe}\end{matrix}>\mathrm{CH_2}$, which crystallises in rhombohedra, melts at 157·5°, is soluble in most organic solvents except light petroleum, and when treated with bromine yields the corresponding *pyridazone*, which crystallises from alcohol in small, colourless needles and melts at 189—190°. On treating the latter with phosphorus oxychloride, it yields 6-*chloro*-3-*phenyl*-5-*methylpyridazine*, which crystallises from alcohol in slender needles, and melts at 141—142°, and, when treated with hydriodic acid, yields 3-*phenyl*-5-*methylpyridazine*, which crystallises in long, silky needles and melts at 95°; the *hydriodide* of the latter crystallises in yellowish-brown needles, sinters at 90°, and is completely molten at 140°, and the *chromate* crystallises in slender, felted needles, The chloropyridazine, when treated with sodium ethoxide, yields 6-*ethoxy*-3-*phenyl*-5-*methylpyridazine*, which crystallises in slender needles, melts at 103—104°, and forms an insoluble *aurichloride*, a *chromate*, and a *picrate* melting at 150°; the analogous 6-*methoxy*-compound crystallises from alcohol in slender, felted needles, and melts at 60—61°; 6-*anilino*-3-*phenyl*-5-*methylpyridazine*, obtained when the chloro-compound is treated with aniline, is a white, crystalline substance which melts at 173—174°, and forms an insoluble *chromate*. R. H. P.

Derivatives of Pyrimidine. By William O. Emery (*Ber.*, 1901, **34**, 4178—4181).—When dialuric acid is heated with phosphorus pentachloride, initially on the water-bath, and finally in a sealed tube for half an hour at 120°, it is converted into the same tetrachloropyrimidine as was formerly obtained in the same way from alloxan (Ciamician and Magnaghi, Abstr., 1886, 226); the latter melts at a temperature slightly higher (70°) than formerly given (67—68°), and is not changed by distilling with zinc dust or by sodium amalgam. When heated with sodium iodide in alcoholic solution for 10 hours, it is converted into a mixture of *trichloroiodopyrimidine*, $C_4N_2Cl_3I$, and *dichlorodiiodopyrimidine*, $C_4N_2Cl_2I_2$; these are separated on recrystallisation from methyl alcohol, the latter being obtained in needles melting at 159°, and the former in yellowish nodules melting at 93—94°.

Tetrabromopyrimidine, $C_4N_2Br_4$, obtained from dialuric acid and phosphorus pentabromide, is volatile with steam, and forms snow-white crystals melting at 165—166°.

When tetrachloropyrimidine is boiled with zinc dust and water for a long period, the whole of the halogen is removed and pyrimidine formed (compare Gabriel and Colman, Abstr., 1899, i, 638).

W. A. D.

Nitroprusside, Ferrocyanide, and Ferricyanide of Antipyrine. By M. C. Schuyten (*Chem. Centr.*, 1901, ii, 1362; from *Handel. van het vijfde Vlaamsch Natuur Geneeskundig Congres, Brugge*, 1901).—These antipyrine salts are readily prepared by processes of double decomposition. The *nitroprusside*, $(C_{11}H_{12}ON_2)_2,H_2Fe(NO)(CN)_5,H_2O$, is a pale brown, amorphous substance, melts at 77—78°, is soluble in water, and has an acid reaction. Aqueous solutions become blue on exposure to air and solutions in acetone green. *Antipyrine ferrocyanide*,

$$(C_{11}H_{12}ON_2)_2,H_4Fe(CN)_6.$$

is a white substance. *Antipyrine ferricyanide*, $(C_{11}H_{12}ON_2)_3H_3Fe(CN)_6$, forms yellow, needle-shaped crystals, and is readily soluble in water.

E. W. W.

Compounds of Antipyrine with Ferric Haloids. By M. C. SCHUYTEN (*Chem. Centr.*, 1901, ii, 1362—1363; from *Handel van het vijfde Vlaamsch Natuur Geneeskundig Congres, Brugge*, 1901).—Antipyrine ferric chloride (Hasse's ferropyrine, *Pharm. Centr.-H.*, **36**, 59), $(C_{11}H_{12}ON_2)_3FeCl_3$, prepared by mixing aqueous or ethereal solutions of ferric chloride and antipyrine, is an orange-yellow powder, which becomes brown at 150°, melts at 205°, and is readily soluble in water. The aqueous solution has an acid reaction, and when warmed gives a brown precipitate which partially redissolves on cooling. The action of many reagents on the aqueous solution of antipyrine ferric chloride is described in the original paper.

Antipyrine ferric bromide and antipyrine ferric iodide cannot be prepared by mixing the components or by double decomposition, and are doubtless unstable under ordinary conditions. E. W. W.

Synthesis of Uracil, Thymin, and Phenyluracil. By EMIL FISCHER and GEORG ROEDER (*Ber.*, 1901, **34**, 4129. Compare this vol., i, 124).—4-Phenyluracil, prepared by the authors from its hydro-compound, was first obtained by Warmington from ethyl benzoylacetate and carbamide (Abstr., 1893, i, 369).

Weidel and Roithner had already obtained 4-methylhydrouracil in an impure form, and hydrouracil has been described under the name of β-lactylcarbamide by Lengfeld and Stieglitz (Abstr., 1893, i, 632).

G. T. M.

Benziminazoles. By OTTO FISCHER and MORITZ RIGAUD (*Ber.*, 1901, **34**, 4202—4209).—*s*-Dimethylphenylenediamine combines readily with aromatic aldehydes at the ordinary temperature with elimination of $1H_2O$; the products are easily hydrolysed into their components, however, by dilute acids and alkalis. The *compound*, $C_{15}H_{16}N_2$, obtained from benzaldehyde, crystallises from methyl alcohol and melts at 102—103°; the *derivative*, $C_{15}H_{16}ON_2$, obtained from salicylaldehyde forms short, colourless prisms and melts at 155°.

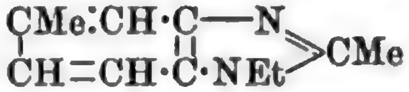
[With W. KOPP.]—1-*Phenylbenziminazole*, $C_{13}H_{10}N_2$, obtained by boiling *o*-aminodiphenylamine with formic acid for several hours, crystallises from light petroleum in concentrically grouped needles and melts at 97°; the *platinichloride* forms reddish-yellow prisms or leaflets, the *mercurichloride* long, pike-shaped crystals, and the *picrate*, slender needles which change into prisms.

The *methiodide*, $C_{14}H_{13}N_2I$, crystallises from water in colourless leaflets, melts at 200°, and with warm aqueous sodium hydroxide yields the carbinol-base, 1-*phenyl-3-methylbenziminazoleol*, $C_6H_4{<}{\substack{NMe \\ NPh}}{>}CH\cdot OH$; this crystallises from dilute alcohol in colourless, flat prisms, melts at 168°, and is only very slowly hydrolysed by boiling aqueous sodium hydroxide. Ultimately, small quantities of an oily *o-methylamino-*

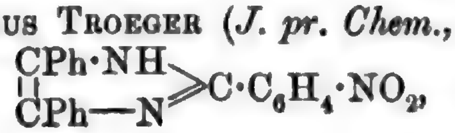
diphenylamine are obtained, the *hydrochloride* of which forms beautiful, colourless needles.

4 : 5-Diamino-*m*-xylene condenses readily with formic acid, giving 4 : 6-*dimethylbenziminazole,* which crystallises from chloroform, on adding light petroleum, in silvery leaflets, melts at 175°, and yields a crystalline *hydrochloride, platinichloride,* and *picrate.* When heated at 130°, with methyl iodide dissolved in methyl alcohol, it yields the 1 : 3 : 4 : 5-*tetramethylbenziminazole methiodide,* $C_{11}H_{15}N_2I$, which crystallises in white needles and melts at 278—279°; the derived *carbinol* base, $C_6H_2Me_2{<}\begin{matrix}NMe\\NMe\end{matrix}{>}CH{\cdot}OH$, crystallises from light petroleum in colourless, acutely truncated prisms, melts at 135°, and is not affected by boiling aqueous alkaline hydroxides.

1 : 4 : 6-*Trimethylbenziminazole iodide* is formed as an easily soluble substance along with the foregoing less soluble, higher methylated derivative, when the parent benziminazole is simply warmed with methyl alcoholic methyl iodide; with potassium hydroxide, it yields a *base* which crystallises from light petroleum in colourless prisms and melts at 70°; the *platinichloride* forms reddish-yellow needles.

p-Nitro-*m*-tolyl ethyl ether crystallises from light petroleum in colourless prisms, melts at 55° (Staedel and Kolb, Abstr., 1891, 186, give 51°), and when heated for 10 hours with alcoholic ethylamine, is converted quantitatively into p-*nitro*-m-*ethyltoluidine,* which crystallises from dilute alcohol in yellowish-red needles and melts at 60°. m-*Ethyl*-o-*tolylenediamine,* obtained by reduction of the nitro-compound with tin and hydrochloric acid, crystallises from light petroleum in long, colourless needles, melts at 59°, and on boiling with acetic acid yields Hübner's 2 : 6-dimethyl-1-ethylbenziminazole (compare O. Fischer and Schilling, Abstr., 1893, 283), which thus has the structure $\begin{matrix}CMe{:}CH{\cdot}C{\cdot}NEt\\ CH{=}CH{\cdot}C{-}N\end{matrix}{>}CMe$. The isomeric 2 : 5-dimethyl-1-ethylbenziminazole is shown to have the structure  $\begin{matrix}CMe{:}CH{\cdot}C{-}N\\ CH{=}CH{\cdot}C{\cdot}NEt\end{matrix}{>}CMe$ by its formation from 4-ethyl-3 : 4-tolylenediamine and glacial acetic acid; it crystallises from light petroleum in long, thin needles, is very hygroscopic and melts at 86—87°, not at 165—166° as stated by Schilling, whose compound probably contained, or consisted of, 3 : 4-*diacetyl*-4-*ethyltolylenediamine,* which melts, when pure, at 177°. The *platinichloride* of the β-azole crystallises in reddish-yellow prisms decomposing at 251°, the *aurichloride* in yellow tufts melting at 129—130°, and the *nitrate* melts at 133°; the *mercurichloride* melts at 190°, whilst the *picrate* forms small, bright yellow prisms, melts at 260—261°, and is very characteristic. The *picrate* of the α-azole melts at 232—233°, and the *mercurichloride* at 149—150°.

On heating the hydrochloride of either the α- or β-azole on the sandbath, ethyl chloride is evolved, and the same ethenyl-3 : 4-tolylenediamine (m. p. 198°) is obtained in both cases; the latter is thus tautomeric according to von Pechmann's views. W. A. D.

Aminolophine. By JULIUS TROEGER (*J. pr. Chem.*, 1901, [ii], **64**, 530—546).—m-*Nitrolophine,*  $\begin{matrix}CPh{\cdot}NH\\ CPh{-}N\end{matrix}{>}C{\cdot}C_6H_4{\cdot}NO_2$, produced together with benzilam from *m*-nitrobenzaldehyde and benzil in presence of ammonia, is a crystalline powder almost insoluble in the ordinary organic solvents, and does not melt at 295°.

m-*Aminolophine*,
$\begin{matrix}\mathrm{CPh{\cdot}NH}\\ \|\\ \mathrm{CPh{-}N}\end{matrix}\!\!>\!\mathrm{C_6H_4{\cdot}NH_2}$, forms minute, thread-like crystals, becomes brown at about 280°, and blackens and melts at 290°; it gives a dirty-white precipitate with phosphotungstic acid, a red-brown precipitate with potassium bismuthoiodide, and a white precipitate with potassium mercuric iodide, a dark yellow precipitate with potassium zinc iodide, a white precipitate with lead acetate, and a dark-brown, crystalline precipitate with iodine in potassium iodide; the *hydrochloride*, $C_{21}H_{17}N_3,2HCl$, separates in needles on adding concentrated hydrochloric acid to a solution of the base in the dilute acid; the *platinichloride*, $(C_{21}H_{17}N_3)_2,H_2PtCl_6$, forms a pale flesh-coloured precipitate; the *nitrate*, $C_{21}H_{17}N_2,HNO_3$, crystallises in needles; the *sulphate*, is only slightly soluble in water, and separates in clusters of crystals; the *picrate*, $C_{21}H_{17}N_3,C_6H_3O_7N_3$, forms brownish-yellow needles, and melts and decomposes at 200°; the *aurichloride* forms a brown precipitate. m-*Aminolophine tetraiodide*, $C_{21}H_7N_3HI_4$, forms brown needles, and decomposes when heated above 200°. The product of the action of methyl iodide on *m*-aminolophine appears to contain loosely combined hydrogen iodide, and the formula

$$C_{21}H_{15}N_3Me_3I,HI,H_2O$$

is provisionally assigned to it.

p-*Aminolophine* crystallises in minute needles and becomes brown and decomposes gradually above 180°; the *hydrochloride*, $C_{21}H_{17}N_3,2HCl$, forms small, compact crystals; the *nitrate* forms white needles, the *platinichloride* is a dirty brown-yellow precipitate, and the *aurichloride* a dark brown precipitate.

o-*Aminolophine* is a white, crystalline substance; the *hydrochloride*, $C_{21}H_{17}N_3,2HCl$, forms minute, white needles. T. M. L.

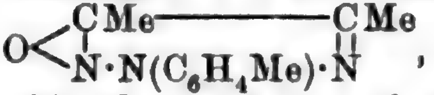
Ketone Reactions of γ-Lutidone. By PAVEL IW. PETRENKO-KRITSCHENKO and S. MOSSESCHWILI (*J. pr. Chem.*, 1901, [ii], **64**, 496).—With phenylhydrazine, γ-lutidone yields a *hydrazone*, $C_{13}H_{15}N_3$, as crystals melting at 125°. With hydroxylamine, an oxime is not formed, but a crystalline *substance*, $C_7H_{10}O_2N$, which melts at 249°.

K. J. P. O.

Partial Hydrolysis of Triaminomesitylene. By FRANZ WENZEL (*Monatsh.*, 1901, **22**, 983—985).—Triaminomesitylene trihydrochloride, when boiled with glacial acetic acid, yields the hydrochloride of *diaminohydroxymesitylene*; the base forms yellow needles, melts at 94—96°, and with acetic anhydride yields the *triacetyl* derivative which has been previously obtained in the endeavour to acetylise triaminomesitylene (Abstr., 1898, i, 580). G. Y.

Oxidation of Hydrazoximes. VI. By GIACOMO PONZIO (*Gazzetta*, 1901, **31**, ii, 413—416. Compare Abstr., 1898, i, 386; 1899, i, 717, 827; 1900, i, 588; 1901, i, 169).—*Diacetyl*-p-*tolylhydrazoxime*, $NOH{:}CMe{\cdot}CMe{:}N_2H{\cdot}C_6H_4Me$, prepared from *iso*nitroso-methyl ethyl ketone (diacetylmonoxime) and *p*-tolylhydrazine, crystallises from alcohol in yellowish prisms melting at 169°, and is soluble in chloroform, benzene, or ether.

4 : 5-*Oxy*-1-p-*tolyl*-3 : 4-*dimethyl*-1 : 2 : 5-*osotriazole*,



obtained by treating a chloroform solution of diacetyl-*p*-tolylhydrazoxime with yellow mercuric oxide under the conditions previously given (*loc. cit.*), crystallises from ether in pale yellow, shining prisms melting at 92—93°, and is soluble in water, light petroleum, alcohol, or chloroform. It is a mono-acid base, and has a weak basic reaction, its hydrochloride being instantly decomposed into its components in contact with water.

Diacetyl-o-tolylhydrazoxime, $C_{11}H_{15}ON_3$, separates from alcohol in faintly yellow, flattened prisms melting at 175° and is soluble in chloroform or ether.

Diacetyl-β-naphthylhydrazoxime, $C_{14}H_{15}ON_3$, crystallises from chloroform in rose-red laminæ melting at 184°, and is soluble in acetone.

T. H. P.

A Solid Diazonium Cyanide; Diazoiodides. By HANS EULER and ARTHUR HANTZSCH (*Ber.*, 1901, **34**, 4166—4169).—On adding concentrated potassium cyanide solution to a solution of anisolediazonium chloride cooled to –80° and prevented from solidifying by the addition of alcohol, the *syn*-cyanide alone is formed, the low temperature apparently failing to influence the equilibrium between the *syn*-diazocyanide and diazonium cyanide; if, however, a solution of anisolediazonium hydroxide, prepared by precipitating a solution of the bromide with moist silver oxide at 0°, be saturated with hydrogen cyanide and concentrated by freezing out and evaporating in a vacuum at 0—5°, crystals of the *diazonium cyanide*,

$$OMe{\cdot}C_6H_4{\cdot}N_2{\cdot}CN,HCN,2H_2O,$$

separate. With a dilution v_{100}, the mol. conductivity is 88, the salt thus electro-chemically resembling potassium cyanide; as it combines instantaneously with β-naphthol, a diazonium group is present. All three possible diazo-forms have thus been realised in the anisole series.

The solid diazo-haloids are to be regarded as solid solutions of colourless diazonium haloids and coloured *syn*-diazo-salts; the explosiveness is proportional to the depth of colour. The chlorides are colourless and not explosive, the bromides slightly, and the iodides strongly, coloured and explosive. The colour of the iodides depends on the temperature of formation, as shown in the case of the following salts precipitated from aqueous methyl alcoholic solutions by lithium iodide.

	At –60°.	At the ordinary temperature.
Anisolediazoiodide..................	Yellowish-white.	Golden-yellow.
p-Bromobenzenediazoiodide	Lemon-yellow.	Orange.
2 : 4-Dibromobenzenediazoiodide.	Golden-yellow.	Dark orange.

W. A. D.

New Method of Producing the Azobenzoic Acids. By JOHANN MAIER (*Ber.*, 1901, **34**, 4132—4134).—The three nitrobenzaldehydes, when heated with excess of aqueous sodium hydroxide solution (40° Be.), are first transformed into molecular proportions of nitrobenzoic acid and nitrobenzyl alcohol, but these products subsequently interact, yielding the corresponding azobenzoic acid, $CO_2H\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CO_2H$.

G. T. M.

The Influence of the Medium, especially of Inorganic Substances, on the Properties of Proteids. By JOHANNES STARKE (*Zeit. Biol.*, 1901, **42**, 187—227).—The influence of the medium (milieu) on the properties of proteids, especially that of heat coagulation, is discussed at length. Another point discussed is the influence of the medium on the solubilities and precipitability of acid and alkali-albumin. The conclusion arrived at is that there is no such influence exercised, but that the proteid molecule is as constant in its properties as other chemically defined substances. W. D. H.

Proteids. II. By ADOLF JOLLES (*Monatsh.*, 1901, **22**, 991—995. Compare Abstr., 1901, i, 490).—The author suggests that the greater the proportion of the total nitrogen of a proteid which, on oxidation, is separated as carbamide, the greater the value of the proteid as a foodstuff. The absorption of nitrogen by the human organism being taken as a guide, it is shown that casein (which yields 73 per cent. of its total nitrogen as carbamide) is utilised to a greater extent than is fibrin (which yields only 45 per cent.). G. Y.

The Aromatic Group of the Proteid Molecule. By VIRGILIO DUCCESCHI (*Beitr. chem. Physiol. Path.*, 1901, **1**, 339—346. Compare Fischer, Abstr., 1901, i, 745, 780).—When proteid is decomposed in hydrochloric acid solution by nitrous acid, cinnamic acid is a constant product. This points to the presence of a phenylalanine group in the proteid molecule. W. D. H.

The Aromatic Group in Gelatin. By KARL SPIRO (*Beitr. chem. Physiol. Path.*, 1901, **1**, 347—356).—Cinnamic acid is obtainable from gelatin as well as from various forms of proteid (see preceding abstract). Nencki has previously shown that phenylethylamine is a product of the putrefaction of gelatin. W. D. H.

Carbohydrate Groups in Albumin from Yolk of Egg. By CARL NEUBERG (*Ber.*, 1901, **34**, 3963—3967. Compare Blumenthal, Abstr., 1899, i, 465, 968).—The albumin from yolk of egg contains a group yielding glucosamine, since, when hydrolysed with hydrobromic acid and the products then oxidised with nitric acid, nor*iso*saccharic acid is formed. This is best isolated in the form of its cinchonine salt (this vol., i, 84). A salt isomeric with cinchonine nor*iso*saccharate is also formed. This is more readily soluble in alcohol, burns brown at 190°, decomposes at 230°, and has $[\alpha]_D +150°$; it is probably identical with *cinchonine* d-*saccharate*. *Quinine* d-*saccharate* melts at 174°, and closely resembles the cinchonine salt. J. J. S.

Serum-albumin of Ox Blood. By A. Hougardy (*Trav. du lab. de L. Fredericq, Liége*, 1901, **6**, 213—223; from *Arch. de Biol.*, **18**).—According to Halliburton, the albumin of ox blood can be differentiated into two fractions by heat coagulation. The main fact is confirmed, but the author doubts whether this is sufficient proof of two different proteids. No other difference between the proteids is alleged to exist. Moreover, a single and total coagulation is obtainable at 65° if that temperature is maintained for 5 or 6 hours. W. D. H.

Serum-globulin. By Prosper van de Kerckhof (*Trav. du lab. de L. Fredericq, Liége*, 1901, **6**, 21—25; from *Arch. de Biol.*, **15**, 640).—The serum-globulin of mammalian blood can be separated by fractional heat coagulation into three (in the dog into four) parts. No other differences are shown to demonstrate that these are separate proteids. No reference is made to recent work, which has shown that serum-globulin can be differentiated by dialysis into euglobulin and pseudoglobulin. W. D. H.

Proteid Chemistry. Part I. A hitherto undescribed Product of Tryptic Digestion. By F. Gowland Hopkins and Sydney W. Cole (*J. Physiol.*, 1901, **27**, 418—428).—The Adamkiewicz reaction depends on the presence of glyoxylic acid in the acetic acid used. During tryptic digestion, a crystalline product is produced which gives the reaction in a typical manner. The substance has the formula $C_{11}H_{12}O_2N_2$; it yields skatole and indole when heated, and gives the pine-splinter reaction directly. The formula corresponds either with an indoleaminopropionic acid, or a scatoleaminoacetic acid, but this requires further investigation. The substance yields also a red derivative with bromine, and is in fact the hitherto unisolated tryptophan.
W. D. H.

Amounts of Hexone Bases obtained from Vegetable Proteids. By Ernst Schulze and Ernst Winterstein (*Zeit. physiol. Chem.*, 1901, **33**, 547—573. Compare Kossel and Kutscher, Abstr., 1901, i, 107).—The yields of histidine, arginine, and lysine obtained by the action of hydrochloric acid on the proteids from the following seeds, have been determined:—*Picea excelsa*, *Pinus silvestris*, *P. maritima*, *Cucurbita Pepo*. Conglutin from the seeds of *Lupinus luteus* and other lupins, legumin from *Pisum sativum*, and edestin have also been hydrolysed and the percentages of bases determined. Except in the case of legumin, the amount of arginine is much greater than that of histidine or lysine, and is at a maximum in the proteid from *Pinus silvestris* and *P. maritima* and in edestin.

The histidine was estimated as its hydrochloride, $C_6H_9O_2N_3,HCl,H_2O$; the arginine as the copper derivative, $(C_6H_{14}O_2N_4)_2,Cu(NO_3)_2,3H_2O$, and the lysine as its platinichloride, $C_6H_{14}O_2N_2,H_2PtCl_6$.

The sum of the percentage of nitrogen present (1) as ammonia, (2) as hexone bases, is always far short of the total percentage of nitrogen present in the phosphotungstic acid precipitate. One source of loss lies in the retention of a certain amount of nitrogen compounds in the precipitate obtained on treating the phosphotungstic acid precipitate with baryta water.

If it is assumed that the amount of arginine produced by the hydrolysis of conglutin with acid is the same as is produced by the action of enzymes on the proteids of the seeds of *Lupinus luteus* during germination, then this amount is greater than that which has been actually found in the germinating plant. J. J. S.

Caseinogen and its Salts. By W. A. Osborne (*J. Physiol.*, 1901, **27**, 398—406).—Caseinogen is an insoluble acid which forms soluble salts not only with potassium, sodium, and calcium, but also with other metallic and organic bases. The calcium salt is the chief proteid ingredient of milk; the ammonium salt is sold as eucasin, the sodium salt as nutrose and plasmon. All the salts are precipitated unchanged by half saturation with ammonium sulphate, full saturation with magnesium sulphate, or excess of alcohol. They liberate free caseinogen on treatment with an acid. They may be divided into two chief groups. Group I contains the calcium, magnesium, barium, and strontium salts; these are precipitated by any finely divided, insoluble substance, and will not pass through the pores of a clay filter. Their solutions are markedly opalescent; they become turbid on warming to 35—45°; this turbidity disappears on cooling. On prolonged heating, they form a film or 'skin' on the surface. They react with the rennin ferment. The caseinogenates of caffeine, strychnine, and other alkaloids belong to this group also, although they do not appear to react with rennin.

Group II contains the salts of potassium, sodium, and ammonium. These are not precipitated by finely divided substances, pass easily through a clay filter, form comparatively clear solutions, do not show the reversible change on warming, do not react with rennin, and no surface film is formed on warming. Lithium caseinogenate belongs to the same group, although it shows a faint turbidity on warming.

Calcium caseinogenate + potassium oxalate gives rise to calcium oxalate + potassium caseinogenate. Potassium caseinogenate + calcium chloride gives rise to calcium caseinogenate + potassium chloride. Certain caseinogenates show hydrolytic dissociation in a marked degree; this increases on warming, and explains the occurrence of the turbidity previously referred to. W. D. H.

A Derivative of Casein containing Sulphur and Chlorine. By Theodor Panzer (*Zeit. physiol. Chem.*, 1901, **33**, 595—608).—When casein is treated with hydrochloric acid and potassium chlorate, freed from excess of chlorine, treated with hydrogen sulphide, air dried, and then extracted for a month with carbon disulphide, the residue is a derivative of casein containing chlorine and sulphur. Its composition is C, 43·14; H, 5·10; N, 10·08; S, 8·86; P, 0·42; Cl, 8·36, and O, 24·04 per cent. It has decided acid properties, yielding *potassium*, *copper*, and *silver* compounds. It dissolves in dilute alkalis, alkali carbonate solutions, also in glacial acetic acid, or in alcohol containing acetic acid, and gives none of the usual proteid reactions. Part of the sulphur is removed on boiling with alkali, and the compound is completely decomposed when boiled with hydrochloric acid. J. J. S.

Separation of Proteoses by Metallic Salts. By Zdenko Černy (*Pflüger's Archiv*, 1901, **87**, 614—633).—The properties of proteoses precipitated by various salts of heavy metals (silver, copper, uranium) are described and compared. The differences observed are believed to be due to the great lability of these substances, and the conclusion is drawn that the different known proteoses as separated by fractional precipitation with neutral salts do not really represent different substances present in the mixture. W. D. H.

Mucin and Mucoids. By FRIEDRICH MÜLLER (*Zeit. Biol.*, 1901, **42**, 468—564).—A lengthy account of several mucins and mucoids. The question to which most attention is directed is the nature of the carbohydrate radicle, the so-called 'animal gum.' It is regarded as probable that it is an acetyl derivative of glucosamine. W. D. H.

Crystallised Cyanohæmoglobin. By RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1901, **33**, 426—450. Compare Abstr., 1900, i, 318).—Crystallised methæmoglobin (Abstr., 1900, i, 196) dissolves in 0·5 per cent. hydrocyanic acid, yielding a reddish solution resembling oxyhæmoglobin and having a characteristic, broad absorption band in the green part of the spectrum. When diluted and mixed with alcohol at −10°, microscopic crystals are obtained; as a rule, these have the shape of long prisms terminated by pyramids, but occasionally are rhomboid in shape. The same compound is obtained by the addition of potassium cyanide to alkaline methæmoglobin solution. It is stable, and may be heated at 40° in a stream of an indifferent gas, or its solution may be boiled at 40° under reduced pressure, without loss of hydrogen cyanide. When heated at 105—110° in a current of dry hydrogen, it loses water and a small amount of hydrogen cyanide; the same gas is evolved when it is boiled with water or acids under atmospheric pressure.

The compound contains 0·158 per cent. of cyanogen, a result which indicates the presence of only one cyanogen group in the molecule (mol. wt. of hæmoglobin = 16669).

The crystals are not affected by light, and bacteria cause only slow putrefication. Treatment with hydrogen sulphide transforms the cyanogen derivative into hæmoglobin.

Back's (*Skand. Arch. Physiol.*, **6**, 299) photomethæmoglobin appears to be identical with cyanohæmoglobin [this has been shown by Haldane, Abstr., 1900, i, 318] and is produced by the action of hydrogen cyanide liberated by the action of sunlight on potassium ferricyanide.

Reduced hæmoglobin does not combine with hydrogen cyanide, but oxyhæmoglobin reacts with hydrocyanic acid solution at 40°, yielding the same cyanohæmoglobin. J. J. S.

Action of Sunlight on Enzymes. By OSKAR EMMERLING (*Ber.*, 1901, **34**, 3811—3814).—The action of sunlight on 1 per cent. solutions of the following enzymes: invertase, yeast-maltase, maize-glucase, lactase, emulsin, and diastase, has been studied. The solutions were exposed for 6 hours and their fermenting properties then tested. With the exception of yeast-maltase, the enzymes suffered but very little deterioration owing to this exposure. Toxins, on the other hand, appear to be very susceptible to light. J. J. S.

The Action of Enzymes on each other. By Augustin Wróblewski, B. Bednarski and M. Wojczyński (*Beitr. chem. Physiol. Path.*, 1901, 1, 289—303).—Pepsin destroys trypsin and hastens the destructive influence of acids; trypsin weakens the action of pepsin, especially in the presence of alkalis; pepsin has no action on rennet; pepsin, trypsin, and diastase have no action on invertin; trypsin and invertin have no action on, but pepsin slightly lessens the action of, diastase; pepsin and trypsin have no action on emulsin. Emulsin is completely 'salted out' by ammonium sulphate, and so differs from invertin. The statement of E. Fischer that emulsin hydrolyses lactose is confirmed. Zymase of yeast is rapidly destroyed by the proteolytic enzyme of the yeast cells. W. D. H.

Tyrosinase. By C. Gessard (*Ann. Inst. Pasteur*, 1901, 15, 593—614. Compare Abstr., 1900, i, 468).—A further study of the colour changes induced by tyrosinase in tyrosine solutions containing various metallic salts shows that the compounds of iron (ferrous sulphate and lactate and ferric chloride) have a specific action, causing the development of a green coloration which changes to blue before the production of the bluish-black precipitate already noticed. This reaction takes place even when the solution has acquired the rose coloration produced in the presence of other metallic salts. Zinc salts, the lactate, for example, give rise to the blue coloration without the production of the intermediate green stage.

The time required for the development of the rose coloration increases very rapidly as the tyrosinase extract is diluted. When the extract is maintained at 65°, the chromogenic property diminishes, until after 30 minutes the tyrosinase is almost wholly destroyed.

Although the metallic salts promote the coagulation of the black precipitate, they hinder the development of the initial coloration, the retardation being proportional to the amount of salt introduced. The neutral salts produce a retardation varying from 23 minutes to 9 days, whilst the addition of an alkali carbonate prevents the development of the coloration for a period of 17 days. Albumin from the egg of the fowl also produces a very notable retardation. The serum of different animals (calf, sheep, pig, horse, mare, and rabbit) exhibits this inhibitive action, but to a less extent; calf serum has the greatest effect, whilst that of the rabbit is least efficacious. The inhibitive action of the rabbit serum is, however, very appreciably increased by repeatedly injecting the animal with an aqueous extract of tyrosinase. G. T. M.

Synthetical Action of Yeast Maltase. By Oskar Emmerling (*Ber.*, 1901, 34, 3810—3811).—A small amount of amygdalin is obtained when a mixture of Fischer's mandelonitrile glucoside (Abstr., 1895, i, 554) and pure dextrose is left in contact with a solution of yeast maltase (Abstr., 1901, i, 258) in sealed tubes for 3 months at 35°. J. J. S.

Organic Chemistry.

Galician Petroleum. I. Nitration of the *iso*Hexane Fraction. By ROMAN ZALOZIECKI and G. FRASCH (*Ber.*, 1902, **35**, 386—391).—By repeated fractionation of Galician petroleum, 42 fractions were obtained between 16° and 101°. The 10 fractions from 45° to 65°, which contain the hexanes, were each nitrated with a mixture of one part of nitric acid of sp. gr. 1·404 and three parts of sulphuric acid of sp. gr. 1·84. The crystalline products thus produced were fractionally crystallised from alcohol and yielded (i) a substance crystallising in long, yellow needles, melting at 89·5° ($N = 19·38$ per cent.), (ii) a much smaller quantity of a substance crystallising in small needles melting at 67° ($N = 19·09$ per cent.), and very small quantities of two other substances crystallising in needles and melting respectively at 65° and 61°. The authors conclude that these nitro-compounds are tertiary trinitrohexanes.

K. J. P. O.

Action of Oxidising Agents on Acetylene. By A. BASCHIERI (*Gazzetta*, 1901, **31**, ii, 461—472).—The portion of this paper referring to the action of fuming nitric acid has already appeared (Abstr., 1900 i, 534).

In either alkaline or acid solution, potassium permanganate oxidises acetylene to carbon dioxide and formic and oxalic acids. With chromic acid, no action takes place, even with very concentrated hot solutions.

T. H. P.

Preparation of Bromoform by Electrolysis. By PAUL COUGHLIN (*Amer. Chem. J.*, 1902, **27**, 63—68).—In the electrolytic production of bromoform from acetone and an alkaline solution of potassium bromide, a better yield is obtained by using sodium carbonate than with sodium hydroxide. The optimum temperature is about 25°, and the current density has a considerable influence on the yield. Too much potassium bromide should not be used and the carbonate should be added only gradually. The yield decreases as excess of acetone is employed. When alcohol was used in place of acetone, only a small amount of bromoform could be obtained.

J. McC.

Transformation of Nitroparaffins. By EUGEN BAMBERGER and ERNST RÜST (*Ber.*, 1902, **35**, 45—53).—The authors point out that not only may nitroparaffins, $R·CH_2·NO_2$, be transformed into *iso*nitroparaffins, $R·CH:NO·OH$, which are recognised as existing in the salts of the nitroparaffins (Michael, Nef, Hantzsch, Holleman, &c.), but also into hydroxamic acids, $R·C(OH):NOH$, and possibly into nitroso-alcohols, $R·CH(OH)·NO$. The decomposition of nitroparaffins into fatty acids and hydroxylamine (Victor Meyer, *Ber.*, 1875, **8**, 29) would then be expressed thus: $R·CH_2·NO_2 \rightarrow R·C(OH):NOH; + H_2O \rightarrow R·CO_2H$

$+ NH_2 \cdot OH$; it is possible that the *iso*nitro-compound is an intermediate stage between the nitroparaffin and the hydroxamic acid.

Acethydroxamic acid was obtained in very small quantity by acidifying with hydrochloric acid an alkaline solution of *iso*nitroethane; after removing the hydrochloric acid with potassium acetate, copper acethydroxamate separated on addition of copper acetate. By a similar method, valerohydroxamic and benzhydroxamic acids were obtained from alkaline solutions of *iso*nitropentane and *iso*phenylnitromethane. From *iso-m*-xylylnitromethane, the hydroxamic acid was not isolated, although the solution gave the characteristic ferric chloride reaction of these acids.

Phenylnitromethane and *o*- and *p*-nitrophenylnitromethane, when treated with sulphuric acid of a certain strength, are converted into the corresponding hydroxamic acids; in the case of the two former nitro-compounds, the hydroxamic acid was only recognised by the ferric chloride reaction; from *p*-nitrophenylnitromethane, *p*-nitrobenzhydroxamic acid (m. p. 176—177°) was isolated. K. J. P. O.

Action of Zinc Ethyl on Nitro- and Nitroso-compounds.

By Arthur Lachman (*J. Amer. Chem. Soc.*, 1901, **23**, 897—902. Compare Dunstan and Goulding, Trans., 1901, **79**, 641—643).—The conclusions arrived at by the author based on the incorrect supposition that triethylamine oxide is formed by the action of zinc ethyl on nitroethane are withdrawn. The mechanism of the action of zinc alkyls on nitro- and nitroso-compounds is discussed, particularly with reference to the work of Bewad (Abstr., 1900, i, 629). E. G.

Action of Organo-magnesium Compounds on Trioxymethylene. Synthesis of Primary Alcohols.

By Victor Grignard and L. Tissier (*Compt. rend.*, 1902, **134**, 107—108).—Trioxymethylene is gradually attacked when boiled with ethereal solutions of organo-magnesium compounds, and the reaction can be utilised as a general method for the preparation of primary alcohols in both the fatty and aromatic series, the yield in a given series being as a rule somewhat higher the lower the molecular weight of the alcohol. The author has prepared propyl alcohol from magnesium ethyl bromide; butyl alcohol from magnesium propyl bromide; *iso*hexyl alcohol from magnesium *iso*amyl bromide; benzyl alcohol from magnesium benzyl bromide, and α-naphthylmethanol from magnesium α-naphthyl bromide.

*iso*Hexyl alcohol boils at 147—148° under 753 mm. pressure, and has a sp. gr. 0·8243 at 0°. It yields an acetate which boils at 159° under 755 mm. pressure, the odours of the acetate and the alcohol being very similar to those of the corresponding amyl compounds.

C. H. B.

Supposed Preparation of Acetol [Acetylcarbinol].

By G. B. Simoncini (*Gazzetta*, 1901, **31**, ii, 496—501).—The supposed formation of acetylcarbinol by the action of moist silver oxide on monobromoacetone is a more complex reaction than was assumed by Emmerling and Wagner (Abstr., 1880, 867). The author has been unable to isolate any trace of the alcohol in this way, but in all cases obtained difficultly separable mixtures of reducing oils of an aldehydic nature. These substances are probably polymerised formaldehydes and acetaldehydes, the formation of which is readily explicable by the ready oxidisability of acetylcarbinol; the latter compound, if formed in the reaction, undergoes instant oxidation under the action of silver oxide. T. H. P.

Studies on Neutralisation. Colorimetric Titrations of Acids and Bases having Complex Functions. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1901, [vii], **25**, 53—59).—A detailed account of work already published (compare Abstr., 1901, i, 497).

G. T. M.

Preparation and Properties of Iminodithiocarbonic Esters. By MARCEL DELÉPINE (*Compt. rend.*, 1902, **134**, 108—110).—To prepare the iminodithiocarbonic esters (Abstr., 1901, i, 518), an alkyl iodide (2 mols.) is added to an alcoholic solution of a primary amine (2 mols.) previously mixed gradually with carbon disulphide (1 mol.). After some time, the liquid is diluted with four or five times its volume of water, and extracted with two or three successive small quantities of ether, which removes unaltered alkyl iodide, thiocyanates, and thiocarbimides and other bye-products. The alcoholic solution is then mixed with sodium hydroxide, which liberates the iminodithiocarbonic ester. The chief reaction is $RNH{\cdot}CS{\cdot}SNH_3R + 2R'I = RN{:}C(SR')_2 + RNH_3I$, and the subsidiary reactions (*a*) $RNH{\cdot}CS{\cdot}SNH_3R + R'I = RNH{\cdot}CS{\cdot}SR' + RNH_3I$, (*b*) $RNH{\cdot}CS{\cdot}SR' = RN{:}C{:}S + SHR'$, (*c*) $SHR' + 2R'I = SR'_3I + HI$.

The iminodithiocarbonic esters have a strong, peculiar odour, and are very mobile, refractive liquids, the lower members of the series being colourless, whilst the higher members have a yellowish tint. The boiling point increases but the sp. gr. decreases as the molecular weight rises, isomerides having, as a rule, the same boiling point and sp. gr., whilst a diminution in the proportion of hydrogen raises the sp. gr. The substitution of $(SEt)_2$ for $(SMe)_2$ raises the boiling point about 20°. The coefficient of expansion is about 0·00085 between 0° and 20°. The esters are soluble in acids but reprecipitated by alkalis, and are neutral to litmus and phenolphthalein but monobasic to methyl orange. All the platinichlorides and most of the picrates, mercurichlorides, and mercuri-iodides are crystallisable.

Constitution.	Sp. gr. 0°/4°.	Boiling point.	Melting point of platinichloride.
$NMe{:}C(SMe)_2$	1·13827	192°	180°
$NEt{:}C(SMe)_2$	1·08477	201	150
$NMe{:}C(SEt)_2$	1·0594	215	161
$NPr{:}C(SMe)_2$	1·0597	219	151
$C_3H_5{\cdot}N{:}C(SMe)_2$	1·10093	220—222	145
$NEt{:}C(SEt)_2$	1·02905	223—224	133
$C_4H_9{}^{\beta}{\cdot}N{:}C(SMe)_2$	1·0262	225	132
$C_5H_{11}{}^{\beta}{\cdot}N{:}C(SMe)_2$	1·0137	242—245	146
$C_5H_{11}{}^{\beta}{\cdot}N{:}C(SEt)_2$	0·97906	260	123
$C_7H_7{\cdot}N.C(SMe)_2$	1·1610 (?)	210—220 (60 mm.)	165

Determinations with the crystallised hydriodide, $C_4H_9 \cdot NS_2,HI$, gave the following results:

Heat of dissolution. $-7 \cdot 45$ Cal.
$C_4H_9NS_2,HI$, diss. + KOH diss. = $C_4H_9NS_2$, liq. + KI, diss. develops + 4·5 Cal.
$C_4H_9NS_2$ liq. + HI diss. = $C_4H_9NS_2,HI$ diss. develops + 9·2 Cal.
$C_4H_9NS_2$ liq. + HI gas = C_4H_9,NS_2,HI cryst. develops + 36·2 Cal.

C. H. B.

Brownish-black Substance obtained by the Action of Zinc Chloride on Acetic Anhydride. By Carlo Montanari (*Gazzetta*, 1901, **31**, ii, 479—496).—By the action of fused zinc chloride on acetic anhydride, Bauer (*Jahresber. Fortschr. Chem.*, 1861, 438) obtained a brown substance to which he assigned the composition $(C_4H_2O)_x$. The author's attempts to prepare this compound have been unsuccessful, substances always being obtained containing a less amount of carbon than required for the formula given above. The author has prepared bromo-derivatives of some of the products obtained by him, and has examined the cryoscopic behaviour of both the original substances and of their bromo-compounds, but has arrived at no conclusion as to their nature. T. H. P.

Condensation Product of Butyric Acid. By Giacomo Albo (*Gazzetta*, 1901, **31**, ii, 473—478).—On keeping a fraction of high boiling point (158—160°) of pure butyric acid for a long time, during part of which it was exposed to direct sunlight, it became transformed into a white, mucilaginous mass, which, after being thoroughly washed with ether and drying, was found to be an amorphous *acid* of the composition $C_{13}H_{22}O_8$. It is soluble in alcohol, alkali solutions, and sulphuric acid, and to a slight extent in water, and decomposes without melting at a temperature higher than 220°. When exposed to the air, the outer layers of the powder become vitreous and transparent. The *silver* salt, $C_{13}H_{19}O_8Ag_3$, is obtained as a flocculent, white precipitate, which is soluble in ammonia solution and quickly blackens on exposure to light. The *copper* salt, $(C_{13}H_{19}O_8)_2Cu_3$, forms a characteristic, pale blue, flocculent precipitate, soluble in ammonia. The *barium* salt is a white precipitate. Titration of the acid with potassium hydroxide yields the normal molecular weight for a tribasic acid. Attempts at esterification have not yet been successful. The author regards the acid as a polymeride of a compound of the simple formula given above. T. H. P.

Halogen Derivatives of the Aliphatic Acids. By Paul C. Freer (*Annalen*, 1901, **319**, 345—357).—A theoretical paper bearing on the following communications in which the influence exerted by the stereoisomerism and orientation of the halogen and carboxyl radicles in the halogen derivatives of aliphatic acids on the physical and chemical properties (electrical conductivity, esterification, hydrolysis, and lactone formation) of these compounds is discussed at considerable length.

G. T. M.

Preparation of the Halogen Derivatives of Butyric and the δ-Halogen Derivatives of Valeric Acids. By A. M. Cloves (*Annalen*, 1902, **319**, 357—368).—α-Chlorobutyric acid is most easily obtained in a pure state by chlorinating ethyl ethylmalonate with the theoretical amount of chlorine, distilling the product in a vacuum, hydrolysing the distillate with alcoholic potassium hydroxide at −10°, and finally heating the chloroethylmalonic acid at 140—150°; it is a colourless, highly refractive liquid boiling at 101·25° under 15 mm. pressure. β-Chlorobutyric acid results from the addition of hydrogen chloride to crotonic acid; there is no tendency to form the α-isomeride in this reaction; the acid boils at 98·5—99·5° under 12 mm. pressure. γ-Chlorobutyric acid, prepared by hydrolysing γ-chlorobutyronitrile with boiling concentrated hydrochloric acid, heating the product at 170—220°, and treating the γ-butyrolactone so obtained with hydrogen chloride at −10°, melts at 16°, and boils with slight decomposition at 115—115·5° under 13 mm. pressure.

This addition of hydrogen chloride is a reversible action and the formation of the chloro-derivative takes place very slowly; the velocity of the direct action is much greater in the case of the production of the corresponding bromo- and iodo-compounds. *δ-Iodovaleric acid* is readily prepared by heating δ-phenoxyvaleric acid with fuming hydriodic acid at 125—130°; it crystallises from light petroleum in colourless prisms and melts at 56—57°.

δ-Chlorovaleric acid, produced by treating the preceding compound with freshly precipitated silver chloride, melts at 18° (compare Funk, Abstr., 1894, i, 34) and distils with partial decomposition at 140—150° under 15 mm. pressure, in this respect differing from its α-, β-, and γ-isomerides.

δ-Valerolactone, formed on heating the δ-chloro-acid at 230—240°, is prepared by boiling δ-iodovaleric acid with alcoholic sodium ethoxide and distilling the product at 215—220°; when pure, it boils at 218—220°.

δ-Bromovaleric acid results from the addition of hydrogen bromide to the preceding lactone, and is also prepared by heating δ-phenoxyvaleric acid with concentrated hydrobromic acid, alkylating the crude product with ethyl alcohol saturated with hydrogen chloride, and hydrolysing the resulting ester with hydrobromic acid; it crystallises from light petroleum in monoclinic prisms and melts at 39—40°. The *ethyl* ester employed in this preparation boils between 120° and 176° under 15 mm. pressure. G. T. M.

Velocity of Esterification and the Electrical Conductivity of α-, β-, γ-, and δ-Halogen Derivatives of Aliphatic Acids. By David M. Lichty (*Annalen*, 1902, **319**, 369—390. Compare Abstr., 1896, ii, 557).—Experiments on the esterification of the α-, β-, γ-, and δ-halogen derivatives of aliphatic acids show that the initial rate of esterification diminishes as the atomic weight of the halogen or the molecular weight of the acid increases; it also decreases when the substituent radicle passes from the α- to the β-position. These differences, however, become less appreciable as the time of experiment is increased, and in those cases where there is no hydrolytic decomposition, the limits of esterification are practically the same. The limiting values, however, are usually vitiated by the hydrolytic changes which are indicated by the presence of chlorine, bromine, or iodine ions in the solutions under observation.

In the case of the γ-substituted acids, the hydrolytic decomposition takes place so rapidly that measurements comparable with those recorded in the α- and β-series cannot be obtained; this is also true, but to a less extent, in the case of the δ-series.

The affinity constant (100 *K*), as measured by the electrical conductivity, decreases considerably as the halogen atom passes from the α- to the β-position, the values for α- and β-chloropropionic acids being 0·1465 and 0·0086 respectively.

In the α-series, this constant diminishes as the molecular weight of the acid increases; the values obtained for chloroacetic, α-chloropropionic, and α-chlorobutyric acid are 0·155, 0·143, and 0·139 respectively. In the β-series, however, the constant for β-chloropropionic is smaller than that for β-chlorobutyric acid. Determinations of the electrical conductivity of the γ-substituted acids indicate that these compounds are very rapidly hydrolysed, the velocity of this change being greatest in the case of the bromo-compounds and least in that of the chloro-derivatives; the molecular conductivity decreases as the atomic weight of the halogen increases.

The affinity constant diminishes as the halogen atom passes from the α- to the δ-position, the values of the coefficients for α-, β-, and γ-chlorobutyric and δ-chlorovaleric acids being 0·1390, 0·0089, 0·0030 (?), and 0·0020 respectively.

The data employed in arriving at these conclusions are exhibited in tabular form, and the communication also contains several series of esterification and conductivity curves. G. T. M.

Action of Superheated Steam on Glycerol Esters of Fatty Acids. By J. Klimont (*Zeit. angew. Chem.*, 1901, **14**, 1269—1270).—In order to determine the relative ease with which various commonly occurring fats are hydrolysed by superheated steam, the fats were heated under various conditions of pressure and time in an autoclave, and the acid number of the fat determined. When heated with water under a pressure of 7 atmospheres for 8 hours, cocoa-nut fat and Japan wax were only very slightly hydrolysed, whilst other fats were considerably attacked; under 15 atmospheres pressure, this difference disappeared. On heating cocoa-nut fat, olive oil, or sesamé oil in a current of steam at 200° for half an hour, the cocoa-nut fat was scarcely affected, and the other two fats only slightly.

The results of the author's experiments are tabulated in the paper.

K. J. P. O.

Synthesis of Derivatives of Ethyl Acetoacetate. By Milorad Z. Jovitschitsch (*Ber.*, 1902, **35**, 151—157).—Improved methods of preparing the following compounds are described: oxime of ethyl acetoacetate, nitrolic acid of ethyl acetate, ethyl chloroiminoacetate, ethyl phenyl*iso*nitrosoglycine, and ethyl phenylazodioxydiazinecarboxylate.

R. H. P.

Action of Methyl Alcohol on Salts of Weak Acids. By Wilhelm Wislicenus and Willi Stoeber (*Ber.*, 1902, **35**, 539—550. See Abstr., 1899, i, 192).—The metallic derivatives of weak acids after prolonged boiling with methyl alcohol or sodium methoxide are often converted into basic methoxides, and these basic methoxides when suspended in boiling benzene are reconverted into the original compounds.

The following *basic methoxides* are described: that from the copper derivative of ethyl α-chloroacetoacetate (small, slender, blue needles decomposing about 180°), that from copper acetate (COMe·O·Cu·OMe, microscopic, blue tablets), that from the magnesium derivative of ethyl acetoacetate. The *copper* derivative of methyl acetophenoneoxalate crystallises from methyl alcohol and melts at 240—241°. The copper derivative of benzoylacetone crystallises in small, bright green needles with MeOH. When an aqueous solution of nickel acetate is shaken with an ethereal solution of ethyl acetoacetate, the *compound*, $C_{20}H_{32}O_{11}Ni_2$, is obtained; this crystallises with EtOH in clusters of silky, greenish needles, and, when boiled with methyl alcohol, yields the *basic methoxide*, $C_7H_{12}O_4Ni$, which crystallises with MeOH and, when boiled with ethyl acetoacetate, yields the *nickel* derivative of ethyl acetoacetate which melts at 228—230°; the analogous cobalt compounds are very similar; the *compound* $C_{20}H_{32}O_{11}Co$ crystallises in compact, ruby-red prisms which decompose at about 200°, the *methoxide* crystallises with MeOH and decomposes at about 135°, and the *cobalt* derivative of ethyl acetoacetate crystallises in red, microscopic needles which melt at about 207°. The *nickel* derivative of ethyl oxalacetate crystallises in small, slender needles and melts at 145°. The *ferric* derivative of benzoylacetone crystallises from benzene and melts at 224—225°; but neither this nor analogous ferric compounds yield basic methoxides. R. H. P.

Double Salts of Cadmium and Mercury. By VOLKMAR KOHLSCHÜTTER (*Ber.*, 1902, **35**, 483—492).—The first of a series of investigations of double salts containing different acid radicles undertaken to test the application of Werner's coordination theory to double salts.

Cadmium oxalate dissolves in a cold saturated solution of potassium chloride, and the solution, after standing for some hours, deposits quadratic crystals of the *salt* $Cd_2[(C_2O_4)_3Cl_2]K_4,6H_2O$. The *bromide*, $Cd_2[(C_2O_4)_3Br_2]K_4,2H_2O$, crystallises in round aggregates of tabular, prismatic crystals, and the analogous *nitrite*, $Cd_2[(C_2O_4)_3(NO_2)_2]K_4,H_2O$, in small, slender, quadratic plates. These compounds may be considered as bimolecular potassium cadmium oxalate, $Cd_2(C_2O_4)_4K_4$, in which one of the oxalic acid radicles has been replaced by Cl_2,Br_2 or $(NO_2)_2$. When cadmium oxalate is dissolved in a solution of ammonium chloride, the *salt* $Cd_4(C_2O_4)_3Cl_{10}(NH_4)_8$ is obtained in quadratic prisms.

The *salt* $Hg_2[(C_2O_4)Cl_6]K_4$ was obtained by a similar method from mercuric oxalate in the form of cubical crystals.

The analogies existing between these compounds are discussed, as also is their constitution. R. H. P.

Synthesis of Organic Acids, Carbohydrates, and Albumin-like Substances. By JULIUS WALTHER (*Chem. Zeit.*, 1901, **25**, 1151).—By the electrolysis of aqueous solutions of carbon dioxide, the author states that he has obtained oxalic, citric, and tartaric acids, and also carbohydrates. In the presence of ammonia or ammonium salts, substances resembling albumin are formed. K. J. P. O.

Doubtful Points in the Application of Mendeléef's Periodic Law. By N. TARUGI and Q. CHECCHI (*Gazzetta*, 1901, **31**, ii, 417—445).—After discussing the positions of argon and of some of the rare earth metals in the periodic classification of the elements, the author gives the following results of his measurements of the solubilities of the succinates, cinnamates, benzoates, and salicylates of magnesium, calcium, strontium, barium, and mercury; the numbers in the table below represent solubilities in percentages:

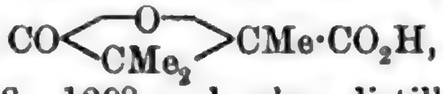
		At 15°.	At 100°.
Magnesium succinate	$(+5H_2O)$	24·3451	66·3593
Calcium „	$(+2H_2O)$	1·2707	0·6615
Strontium „	(monoclinic)	0·4392	0·2145
Barium „		0·4009	0·2060
Mercury „	$C_4H_5O_4Hg$? (amorphous)	—	?
Magnesium benzoate	$(+4H_2O)$	5·8	16·4
Calcium „		8·6	10·2
Strontium „		5·2	5·6
Barium „	$(+6H_2O)$	4·3	10·1
Mercury „	$(C_6H_5{\cdot}CO_2)_2Hg$? (amorphous)	1·2	2·5
Magnesium cinnamate	$(+H_2O)$	0·847	1·94
Calcium „	$(+3H_2O)$	0·21	1·15
Strontium „	$(+2H_2O)$	1·18	3·11
Barium „	$(+2H_2O)$	0·726	2·27
Mercury „	$(CHPh{\cdot}CH{\cdot}CO_2)_2Hg$?	—	0·527
Magnesium salicylate	$(+4H_2O)$	20·40	79·68
Calcium „	$(+3H_2O)$	2·29	35·75
Strontium „	$(+2H_2O)$	3·04	20·44
Barium „	$(+H_2O)$	26·85	54·08

It will be seen that, except in the case of the succinates, the different salts of any one of these acids exhibit properties which do not vary in any regular way with the atomic weights of the metals.

T. H. P.

Synthesis of Dimethylsuccinic Acid under the Action of Light. By W. SERNOFF (*Bull. Soc. Chim.*, 1902, [iii], **27**, 14—16).—On shaking the ethyl ester of α-iodopropionic acid in alcoholic solution with metallic mercury, while exposed to direct sunlight, mercuric iodide separates, and a mixture of the ethyl esters of the two dimethylsuccinic acids is produced.

A. F.

Bromotrimethylsuccinic Acid and the β-Lactone of Trimethylmalic Acid. By GUSTAV KOMPPA (*Ber.*, 1902, **35**, 534—535. See Abstr., 1899, i, 419, and compare Bone and Sprankling, Trans., 1902, **81**, 50).—A mixture of bromotrimethylsuccinic acid and its anhydride, when treated with moist silver oxide, yields the *β-lactone* of *trimethylmalic acid*,  $CO{<}\overset{O}{\underset{CMe_2}{}}{>}CMe{\cdot}CO_2H$, which crystallises in flat needles, melts at 118—120°, and, when distilled, yields a crystalline compound melting at 66—67°, probably the anhydride of trimethylhydroxysuccinic acid.

R. H. P.

Physical Constants of α-Ethylideneglutaric Acid. By FRITZ FICHTER and BENNO MÜHLHAUSER (*Ber.*, 1902, **35**, 341).—The equivalent electrical conductivities of sodium β-ethylideneglutarate in solutions where $v = 32L$ and $1024L$ differ by 11·9 units and not by 20 units as calculated from Ostwald's rule. This constant has also been determined for sodium α-ethylideneglutarate and is found to be 16·4 or 15·5 when calculated in Siemens' reciprocal units. The dissociation constant K of α-ethylideneglutaric acid is 0·0032, which agrees with the value 0·00281 observed for β-methyl-α-ethylideneglutaric acid.

G. T. M.

Action of Semicarbazide on Diacetyl. By OTTO DIELS (*Ber.*, 1902, **35**, 347—351).

—*Diacetylmonosemicarbazone*,

$$CH_2{:}C(OH)\cdot CMe{:}N\cdot NH\cdot CONH_2,$$

obtained by mixing together ice cold aqueous solutions of diacetyl and semicarbazide hydrochloride or the free base, separates from water in leaflets, and from glacial acetic acid in fusiform crystals; it melts and decomposes at 234—235° (corr.). The substance is a weak acid and dissolves in sodium hydroxide solution, the sodium salt separating out on concentration in yellowish-white needles. The salts are, however, dissociated by water and the semicarbazone itself is hydrolysed by warm mineral acids. When boiled with dilute acetic acid, the monosemicarbazone decomposes into diacetyl and diacetyldisemicarbazone.

Diacetylmonoacetylhydrazone, $CH_2{:}C(OH)\cdot CMe{:}N\cdot NHAc$, is produced either by boiling diacetylmonosemicarbazone with acetic anhydride or by the interaction of diacetyl and acetylhydrazine in aqueous solutions; it crystallises from acetone in white needles melting at 166°. The hydrazone sublimes at temperatures below 100° and may be distilled without decomposition; it behaves as a weak acid, its concentrated sodium hydroxide solution yielding the sodium salt. The alkaline solutions of the hydrazone, when boiled, become turbid and deposit dimethylaziethane. With dilute hydrochloric acid, the hydrazone yields its hydrochloride; the stronger acid, however, hydrolyses it into its generators.

G. T. M.

Inversion of Sucrose. By PAUL PETIT (*Compt. rend.*, 1902, **134**, 111—112).

—Direct determinations of the heat developed by the inversion of sucrose by dilute sulphuric acid give 2·639 Cal. at 58·5° and 2·675 Cal. at 63°, the probable value at 15° being 2·3 Cal. This value is lower than that obtained by Brown and Pickering (Trans., 1897, **71**, 783) for inversion by sucrase, but their determinations were made with comparatively small quantities of material.

C. H. B.

Composition of Molasses from Pale Peat. By HUGO BORNTRÄGER (*Zeit. anal. Chem.*, 1901, **40**, 787—789).

—The author communicates analyses by different chemists of three specimens of the saccharine substance obtained from peat by his process (D.R.-P. 122193; see also this vol., ii, 187). Although the results of the three analyses are somewhat differently expressed, they agree in showing 22 per cent. of reducing sugar (calculated as dextrose) in the dry substance.

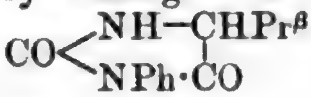
M. J. S.

Effect of Prolonged Boiling of Aqueous Solutions of Glycogen. By JOSEPH NERKING (*Pflüger's Archiv*, 1901, **88**, 1—6. Compare Pflüger, *ibid.*, 1899, **75**, 120).—When aqueous solutions of glycogen are boiled for several days, the total amount of carbohydrates, when estimated by the cuprous oxide method after hydrolysis, remains the same, although appreciable amounts become transformed into carbohydrates soluble in alcohol. For example, after boiling for 12 days, 3·76, and for 14 days, 4·81 per cent. of the original carbohydrate becomes soluble. Similar effects are produced when glycogen is boiled with very dilute (0·1 per cent.) solutions of lactic acid, but are brought about much more readily. J. J. S.

Preparation of Xylan. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1901, **34**, 162—180).—For the preparation of xylan, wheat straw is hydrolysed with 6 per cent. sodium hydroxide solution, filtered, and the xylan precipitated by the aid of Fehling's solution. The precipitate is triturated with dilute hydrochloric acid, then mixed with alcohol, washed with alcohol, and finally with ether. The yield is 22—23 per cent. of the straw. The composition agrees best with the formula $C_{10}H_{18}O_9$, whereas Tollens has previously ascribed the formula $C_5H_8O_4$ to the compound. The specimen did not contain araban, mannan, or galactan, but small amounts of silica and cellulose were present as impurities. J. J. S.

Aminovaleric Acids. By MAX D. SLIMMER (*Ber.*, 1902, **35**, 400—410).—*a*-Amino*iso*valeric acid (Clark and Fittig, *Annalen*, 1866, **139**, 200) was prepared by heating *a*-bromo*iso*valeric acid with a saturated solution of ammonia and ammonium carbonate under pressure at 100°; it melted and decomposed at 298° (corr.). The *ethyl* ester is an oil boiling at 63·5° under 8 mm. pressure, and at 174° with decomposition under atmospheric pressure, and having a sp. gr. 0·9617 at 15°/4°; the *picrate* of the ester forms small, yellow crystals melting at 139·5° (corr.); the *hydrogen tartrate* crystallises in prisms, and yields an amino-acid which is optically active. When kept, the ethyl ester changes to a solid, crystalline substance. *a-Benzoylaminoisovaleric acid*, $NHBz\cdot CHPr^{\beta}\cdot CO_2H$, crystallises in leaflets melting at 132·5° (corr.).

With phenylcarbimide, *a*-amino*iso*valeric acid yields a substituted *phenylcarbamide*, $NHPh\cdot CO\cdot NH\cdot CHPr^{\beta}\cdot CO_2H$, which crystallises in colourless leaflets melting and decomposing at 163·5° (corr.), and is converted by boiling with hydrochloric acid into *phenylisopropylhydantoin*,

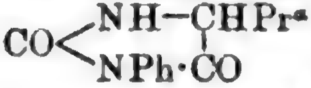


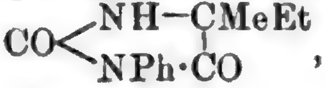
$$CO<\begin{array}{l}NH-CHPr^{\beta}\\ \qquad\quad | \\ NPh\cdot CO\end{array}$$

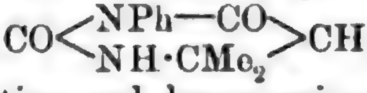
; this forms long needles melting at 124—125° (corr.).

a-Aminovaleric acid was prepared from *a*-bromovaleric acid and melts and decomposes at 291·5° (corr.); the *ethyl* ester boils at 68·5° (corr.) under 8 mm. pressure and has a sp. gr. 0·9447 at 15°/4°; its *picrate* melts at 115·6° (corr.). *a-Benzoylaminovaleric acid*,

$$NHBz\cdot CHPr^{a}\cdot CO_2H,$$

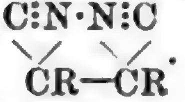
prepared from the acid or the ethyl ester, melts at 152·5° (corr.). With phenylcarbimide, *a*-aminovaleric acid gives a *phenylcarbamide*, $NHPh\cdot CO\cdot NH\cdot CHPr^{a}\cdot CO_2H$, which crystallises in leaflets melting and decomposing at 119° (corr.), and yields *phenylpropylhydantoin*,  $CO<\begin{matrix}NH-CHPr^{\alpha}\\NPh\cdot CO\end{matrix}$, melting at 102° (corr.).

a-Amino-a-methylbutyric acid, $NH_2\cdot CMeEt\cdot CO_2H$, was prepared by heating methyl ethyl ketone with anhydrous hydrogen cyanide under pressure at 80°; the product is dissolved in alcoholic ammonia, and the solution, after a considerable interval, neutralised with hydrochloric acid; the acid crystallises in minute prisms melting at 307·5° (corr.); the *copper* salt crystallises, with $3H_2O$, in blue leaflets; the *ethyl* ester boils at 65—66° under 20 mm. pressure and yields a *picrate* which crystallises in leaflets melting at 115—116°. *a-Benzoylamino-a-methylbutyric acid*, $NHBz\cdot CMeEt\cdot CO_2H$, melts at 198—199° (corr.). The *phenylcarbamide* derivative, $NHPh\cdot CO\cdot NH\cdot CMeEt\cdot CO_2H$, forms crystals melting and decomposing at 179—180° (corr.), and yields *phenylmethylethylhydantoin*,  $CO<\begin{matrix}NH-CMeEt\\NPh\cdot CO\end{matrix}$, crystallising in long needles melting at 118° (corr.).

β-Amino*iso*valeric acid was prepared by heating dimethylacrylic acid with aqueous ammonia under pressure at 150°; the *ethyl* ester boils at 75° under 22 mm. and at 170° under 760 mm. pressure and has a sp. gr. 0·8165 at 20°/4°; its *hydrochloride* is hygroscopic and melts at 75°. *β-Benzoylaminoisovaleric acid*, $NHBz\cdot CMe_2\cdot CH_2\cdot CO_2H$, crystallises in leaflets melting at 141·5°. The *compound* with phenylcarbimide, $NHPh\cdot CO\cdot NH\cdot CMe_2\cdot CH_2\cdot CO_2H$, crystallises in needles melting at 137° (corr.), and when boiled with hydrochloric acid, yields 1-*phenyl-4-dimethylhydrouracil*,  $CO<\begin{matrix}NPh-CO\\NH\cdot CMe_2\end{matrix}>CH_2$, which crystallises in long, colourless needles melting and decomposing at 237°.

K. J. P. O.

Synthesis of an Isomeride of Leucine. By Alexandre Étard and A. Vila (*Compt. rend.*, 1902, **134**, 122—124).—Active valeraldehyde, $CH_2Me\cdot CHMe\cdot CHO$, when treated with ammonia of sp. gr. 0·950, yields the calculated quantity of the ammonia compound, $C_5H_{10}O,NH_3,8H_2O$, in white, optically active crystals, and this, when dried and treated with dry hydrogen cyanide, yields the calculated quantity of an oily cyanogen derivative, $C_{12}H_{18}N_2$, which boils at 115—120° under 30—40 mm. pressure, combines directly with a molecular proportion of bromine, and seems to have the constitution

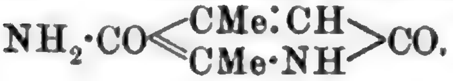


. When hydrolysed with sulphuric acid, it yields a leucine, which crystallises very readily, has a persistent, sweet taste, and a solubility of 5·8 in 100 at 18°. It is not identical with the leucine of animal tissues, and contains two asymmetric carbon atoms.

C. H. B.

Acetoacetamide. By Ludwig Claisen and K. Meyer (*Ber.*, 1902, **35**, 583—584).—*Acetoacetamide*, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot NH_2$, may be obtained by leaving ethyl acetoacetate in contact with 10 per cent. aqueous ammonia for several weeks, extracting the product with ether, and evaporating the aqueous solution under diminished pressure. It forms colourless crystals melting at 50°, and is readily soluble in water or alcohol, but insoluble in ether. Its *copper* derivative, $(C_4H_6O_2N)_2Cu$, forms green crystals. The *phenylhydrazone*, $N_2HPh{:}CMe{\cdot}CH_2{\cdot}CONH_2$, melts at 128° and, in contact with mineral acids, yields 1-phenyl-3-methylpyrazolone. The *phenylazo*-derivative, $N_2HPh{:}CAc{\cdot}CONH_2$, forms yellow crystals melting at 151°.

When heated, acetoacetamide is converted into the *amide* of Nieme and Pechmann's lutidonecarboxylic acid (Abstr., 1891, 675),



$$NH_2{\cdot}CO{<}\begin{matrix}CMe{:}CH\\CMe{\cdot}NH\end{matrix}{>}CO.$$

J. J. S.

Occurrence of Cyanogen Compounds in Coal-Gas, and of the Spectrum of Cyanogen in that of the Oxy-Coal-Gas Flame. By WALTER NOEL HARTLEY (*Sci. Proc. Roy. Dublin Soc.*, 1901, **9**, 289—297).—A reply to certain criticisms passed by Eder and Valenta on the author's previous work (*Phil. Trans.*, 1894, **185**, 16). It is pointed out that Eder and Valenta, working on the same subject, burned the gas in a different manner; further, the Dublin gas supply has been shown to contain cyanogen compounds in sufficient quantity to account for the cyanogen spectrum obtained. J. C. P.

Quadrivalent Oxygen. By KENDAL C. BROWNING (*Ber.*, 1902, **35**, 93).—Attention is drawn to the fact that the compound of ferrocyanic acid and ether (Trans., 1900, **77**, 1233) is formed with development of heat from dry ferrocyanic acid and ether; it was previously regarded by the author as a compound in which oxygen was quadrivalent (compare Baeyer and Villiger, Abstr., 1901, i, 659).

K. J. P. O.

Action of Potassium Cyanide on Cuprous Thiocyanate. By HERRMANN ITZIG (*Ber.*, 1902, **35**, 106—110).—Cuprous thiocyanate dissolves in a boiling 10 per cent. solution of potassium cyanide, and on cooling the solution a complex cyanide, $KCN,Cu_2(CN)_2,H_2O$, separates, identical with that obtained by Schiff and Becchi (*Annalen*, 1866, **138**, 25). From the mother liquor crystallises, first, the salt, $2KCN,Cu_2(CN)_2$, described by Rammelsberg (*Ann. Phys. Chem.*, 1859, **106**, 491), and finally a *thiocyanocyanide*, $Cu_2(CN)_2,4KCN,2KCNS,H_2O$, which forms microscopic needles very soluble in water. With aqueous copper sulphate, its solution gives at first a pale yellow precipitate which, on further addition of copper sulphate, becomes finally bluish-black; with mercuric chloride, a white, crystalline precipitate,

$$3(KCN,CuCN),2(Hg[CN]_2,KCNS),$$

is produced which is fairly soluble in water.

Mercuric thiocyanate, when boiled with aqueous potassium cyanide, yields the complex salt $Hg(CN)_2,KCNS$, obtained by Boekmann (*Annalen*, 1837, **22**, 239) and Cleve (*Bull. Soc. Chim.*, 1875, [ii], **23**, 71).

K. J. P. O.

Acetylenoid Metallic Radicles. By MARCELLIN P. E. BERTHELOT (*Ann. Chim. Phys.*, 1902, [vii], **25**, 65—67).—An account of work already published, including a discussion of the results obtained by Chavastelon (Abstr., 1900, i, 324, 470; 1901, i, 494). G. T. M.

Stereochemistry of Benzene. By CARL GRAEBE (*Ber.*, 1902, **35**, 526—531).—A discussion of various representations of the space formula of benzene. A new figure is favoured and is obtained by joining up by two edges three pairs of tetrahedra joined by two apices. This is practically a representation in space of the Kekulé formula and satisfactorily explains the following facts: that phthalic acid, but not *iso*phthalic acid, forms an anhydride, that catechol alone of the dihydroxybenzenes forms a methylene ether and a carbonate, that two hydrogen atoms in benzene have never been replaced by one bivalent atom, that only one naphthalene or one fluorene, &c., is known, that such compounds as 1 : 8-naphthalene oxide are unknown. Like the Kekulé formula, however, it does not readily explain the identity of 1 : 2- and 1 : 6-disubstitution derivatives of benzene. R. H. P.

Influence of different Atoms and Atomic Groups on the Conversion of Aromatic Sulphides into Sulphones. By J. J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, **4**, 264—266).—The steric influence of groups in the ortho-position in aromatic sulphides on the conversion of the latter into sulphones by means of nitric acid of sp. gr. 1·52 was investigated. Picryl sulphide, 3 : 5 : 3′ : 5′-tetranitro-*o*-tolyl sulphide, and 2 : 2′-dicyano-4 : 6 : 4′ : 6′-tetranitrophenyl sulphide, that is, symmetrically trisubstituted sulphides, are not oxidised by nitric acid, but 2 : 4 : 2′ : 4′-tetranitrophenyl sulphide and *s*-trinitrothioanisole are readily converted into sulphones. The *sulphone* obtained from trinitrothioanisole melts at 218°. K. J. P. O.

Triphenylmethyl. Correction. By FRIEDRICH KEHRMANN (*Ber.*, 1902, **35**, 622. Compare this vol., i, 89).—Gomberg was the first to suggest the quinonoid structure for so-called triphenylmethyl, and not Norris and Sanders as previously stated. J. J. S.

Acetylation of Aromatic Amines. By BRONISLAW PAWLEWSKI (*Ber.*, 1902, **35**, 110—113, 622. Compare Abstr., 1898, i, 362).—Thioacetic acid is shown to be generally applicable for the acetylation of aromatic amines. *Diacetyldianisidide*, hitherto undescribed, crystallising in small leaflets melting at 242—243°, was prepared.

The method is especially applicable in the case of the aminobenzoic acids. K. J. P. O.

Affinity Constants of certain Nitroamines and *iso*Nitroamines. By ARTHUR HANTZSCH [and, in part, M. BUCHNER] (*Ber.*, 1902, **35**, 265—268. Compare Baur, Abstr., 1897, ii, 546).—Perfectly pure, colourless phenylnitromethane (Bamberger, Abstr., 1893, i, 326) is unimolecular in benzene solution and its affinity constant $K = 0·0023$ at 25°. The corresponding *iso*nitroamine, nitrosophenylhydroxylamine, has the constant $K = 0·00046—0·00057$ at 0°, and for nitrosobenzylhydroxylamine, $C_6H_5·CH_2·N(NO)·OH$, $K = 0·000583$ at 0° and 0·000645 at 25°.

The constant for phenylnitroamine rises rapidly with the temperature, a characteristic feature of pseudo-acids which undergo ionising isomerism.

J. J. S.

Condensation of Aldehydes with Methylamine and Ethylamine and Reduction of the Condensation Products. By CARL ANDREE (*Ber.*, 1902, **35**, 420—425).—*Piperonylenemethylamine*,

$CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}NMe$,

a white, waxy substance, melts at 46°, boils at 148° under 16 mm pressure, and is readily decomposed by dilute acids. *Piperonylmethylamine*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}NHMe$, is a colourless oil, which boils at 146° under 12 mm. pressure, and is insoluble in water; the *hydrochloride* forms small, silvery flakes, dissolves readily in water, and melts at 191°; the *hydrobromide* forms white scales, dissolves readily in water, and melts at 191°; the *platinichloride* crystallises from alcohol in minute, yellow needles, and melts at 182° with frothing and decomposition; the *picrate* crystallises from alcohol in minute needles and melts at 154°.

Piperonylene-ethylamine, $CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}NEt$, melts at 51° and is readily hydrolysed. *Piperonylethylamine*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}NHEt$, is a colourless oil and boils at 148° under 20 mm. pressure; the *hydrochloride* forms thin, silky flakes, and decomposes and melts at 201°; the *hydrobromide* forms silky flakes and melts at 184—185°; the *platinichloride* forms red needles and melts and decomposes at 192°; the *picrate* crystallises from absolute alcohol in minute, yellow needles and melts at 157°; the aurichloride could not be obtained owing to the separation of metallic gold.

Cinnamylidenemethylamine, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}NMe$, is an oil which boils at 134—141° under 16 mm. pressure, and was on one occasion obtained as a crystalline solid. *Hydrocinnamylmethylamine*,

$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NHMe$,

is a colourless oil which boils at 133—135° under 18 mm. pressure; the *hydrochloride* and *hydrobromide* were not analysed; the *platinichloride* forms yellow flakes and melts at 181—182°; the *aurichloride* is an oil; the *picrate* forms yellow needles and melts at 93—94°.

Cinnamylidene-ethylamine, $C_{11}H_{13}N$, is a brown solid and boils at 143—145° under 20 mm. pressure. *Hydrocinnamylethylamine*, $C_{11}H_{17}N$, is an oil which boils at 124—126° under 25 mm. pressure; the *platinichloride* crystallises in yellow needles and melts at 134—135°; the *aurichloride* and *picrate* were obtained as oils.

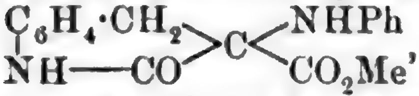
o-*Nitrobenzylidenemethylamine*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}NMe$, is an oil which boils at 145° under 23 mm. pressure. o-*Nitrobenzylidene-ethylamine* is an oil which decomposes when distilled even under reduced pressure.

T. M. L.

Esters of Anilinomalonic Acid and their Derivatives. By MAX CONRAD and H. REINBACH (*Ber.*, 1902, **35**, 511—525. Compare Abstr., 1898, i, 589).—*Methyl anilinomalonate* separates from acetic acid in large, rhombic crystals, melts at 68°, and yields a *hydrochloride* which melts at 133—135°, undergoing decomposition into carbon dioxide, methyl chloride, methyl alcohol, and diphenyldiketopiperazine; the *amide* crystallises in long, white prisms and melts at 156°. *Anilinomalonic acid* crystallises in colourless needles, melts and decomposes at

118—119°, and forms insoluble *calcium*, *silver*, *lead*, *zinc*, and *copper* salts, and an *aniline* salt, which crystallises in colourless, lustrous prisms melting and decomposing at 119°.

The remaining methylenic hydrogen atom in anilinomalonic acid is replaceable by sodium, giving compounds which react with alkyl haloids. *Methyl anilinomethylmalonate*, $NHPh\cdot CMe(CO_2Me)_2$, crystallises from benzene or alcohol and melts at 97°, and the corresponding *amide* crystallises from water, softens at 183°, and melts at 187°. *Methyl anilinobenzylmalonate* crystallises in white prisms and melts at 94°. *Methyl* o-*nitrobenzylanilinomalonate* forms colourless prisms, melts at 157°, and, when reduced, yields *methyl 2-anilinohydrocarbostyril-2-carboxylate*,

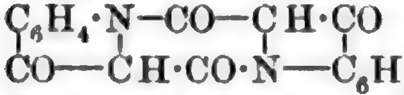


$\begin{array}{l}C_6H_4\cdot CH_2\\ NH—CO\end{array}\!>C<\!\begin{array}{l}NHPh\\ CO_2Me\end{array}$, which melts at 171° and dissolves in hydrochloric acid, but is reprecipitated by water. 2-*Anilinohydrocarbostyril* crystallises from acetic acid and melts at 178°. *Methyl anilinoethylenetricarboxylate*, $NHPh\cdot C(CO_2Me)_2\cdot CH_2\cdot CO_2Me$, crystallises from methyl alcohol and water and melts at 95°.

The anilinomalonates condense with the esters of unsaturated acids, forming substituted pyrrolidonedicarboxylates. *Ethyl* 1 : 4-*diphenylpyrrolidone*-5 : 5-*dicarboxylate* melts at 99°, the corresponding *methyl* ester crystallises in hard prisms melting at 130°, and the *acid* in prisms which melt and decompose at 178°. The monocarboxylic *acid*, obtained by heating the dibasic acid at 180°, melts at 147° and forms a *silver* salt which crystallises in small, slender needles.

The action of bromine on methyl anilinomalonate yields *methyl* p-*bromoanilinomalonate*, which crystallises in clusters of colourless needles melting at 84°. *Methyl dianilinomalonate* crystallises from methyl alcohol and melts at 124—125°.

The esters of anilinomalonic acid, when heated, condense with the formation either of indoxylates (see Blank, *loc. cit.*) or of derivatives of 2 : 5-diketopiperazine of the type of diindoxylic anhydride,



$\begin{array}{l}C_6H_4\cdot N—CO—CH\cdot CO\\ CO—CH\cdot CO\cdot N—C_6H_4\end{array}$, which may be also prepared by prolonged heating of the indoxylates. *Diindoxylic anhydride* crystallises in lustrous, bright yellow leaflets and does not melt below 290°; and the p-*tolyl* (yellow, crystalline, insoluble powder) and the β-*naphthyl* derivatives are described.

Dibromobarbituric acid, when heated with aniline, is converted into the monobromo-acid. R. H. P.

Transformation of Imino-ethers into Acid Amides. By WILHELM WISLICENUS and HEINRICH KÖRBER (*Ber.*, 1902, **35**, 164—168).—A further discussion of results previously obtained (Abstr., 1900, i, 435). The transformation of benzimino-β-chloroethyl ether into β-chloroethylbenzamide, first observed by Gabriel and Neumann (Abstr., 1892, 1331), is now shown to conform with the general rule for such transformations given by Wheeler and Johnson (Abstr., 1900, i, 293).

R. H. P.

Tribromophenol Bromide. By J. H. KASTLE [with A. S. LOEVENHART, ROSA SPEYER, and J. W. GILBERT] (*Amer. Chem. J.*, 1902, **27**, 31—52).—*Tribromophenol bromide*, described by Benedikt (Abstr., 1879, 717), is obtained by the action of bromine on aqueous phenol in yellow crystals (m. p. 118°). The molecular weight determined cryoscopically, using ethylene bromide as solvent, corresponds with that required for the formula $C_6H_2OBr_4$. By the action of heat, of light, or of iodine in carbon disulphide solution, it gives *hexabromophenoquinone*, $C_{12}H_{42}OBr_6$. This same substance has been obtained from tribromophenol and silver tribromophenoxide. When heated in a sealed tube at 100° with water, tribromophenol bromide gives a mixture of tribromophenol and tetrabromoquinone; with dry potassium iodide, it gives hexabromophenoquinone, but in aqueous solution potassium tribromophenoxide is produced. Its rate of decomposition is greatly accelerated by the presence of free bromine. Zinc ethyl gives with it zinc tribromophenoxide and ethyl bromide, and this is evidence that the constitution ($C_6H_2Br_3{\cdot}OBr$) suggested by Benedikt is incorrect. To further prove the incorrectness of Benedikt's formula, it has been shown that tribromophenyl benzenesulphonate, $C_6H_5{\cdot}SO_2{\cdot}OC_6H_2Br_3$ (m. p. 99°), prepared by the action of sodium tribromophenoxide on benzenesulphonic chloride, cannot be obtained from tribromophenol bromide and sodium benzenesulphinate, but that the latter reaction again gives rise to hexabromophenoquinone. With silver nitrate solution, tribromophenol bromide gives *m*-dibromoquinone, and this reaction, as well as the others, can be explained by the formula suggested by Thiele and Eichwede (Abstr., 1900, i, 288). Tribromophenol bromide, when treated with sulphuric acid, suffers a molecular rearrangement and tetrabromophenol is formed. The analogous trichlorophenol bromide does not suffer a corresponding change. This rearrangement is explained on the basis of Thiele's theory of partial valency (Abstr., 1899, i, 554).

J. McC.

Bromides of Eugenol and of *iso*Eugenol. By KARL AUWERS and O. MÜLLER (*Ber.*, 1902, **35**, 114—124).—Bromo*iso*eugenol dibromide, $OH{\cdot}C_6H_2Br(OMe){\cdot}CHBr{\cdot}CHMeBr$, is not soluble in dilute alkalis, but behaves as a pseudo-phenol; with aqueous acetone, it yields *β-m-dibromo-a-hydroxydihydroisoeugenol*,

$$OH{\cdot}C_6H_2Br(OMe){\cdot}CH(OH){\cdot}CHMeBr,$$

which crystallises from glacial acetic acid and melts at 135—136°. With cold methyl alcohol, the dibromide gives the *methyl* ether,

$$OH{\cdot}C_6H_2Br(OMe){\cdot}CH(OMe){\cdot}CHMeBr,$$

which forms stout, colourless crystals and melts at 104—105°; the corresponding *ethyl* ether crystallises from alcohol and melts at 78—80°. The *acetate*, $OH{\cdot}C_6H_2Br(OMe){\cdot}CH(OAc){\cdot}CHMeBr$, obtained by adding sodium acetate to a boiling solution of the dibromide in glacial acetic acid, is a bright yellow, transparent, waxy substance; its *benzoyl* derivative, $C_{19}H_{18}O_5Br_2$, crystallises from alcohol and melts at 112—114·5°.

The foregoing methyl ether melting at 104—105° is readily converted by boiling methyl alcoholic sodium methoxide into *bromo-aβ-dimethoxydihydroisoeugenol*, $OH{\cdot}C_6H_2Br(OMe){\cdot}CH(OMe){\cdot}CHMe{\cdot}OMe$, both bromine atoms of the dibromide being replaced by methoxyl groups; the product separates from alcohol in stout, colourless crystals, melts at 81—83°, and yields a *benzoyl* derivative which forms colourless crystals melting at 92—93°. *Bromo-α-hydroxy-β-methoxydihydroisoeugenol*, $OH\cdot C_6H_2Br(OMe)\cdot CH(OH)\cdot CHMe\cdot OMe$, obtained similarly from the corresponding alcohol,

$$OH\cdot C_6H_2Br(OMe)\cdot CH(OH)\cdot CHMeBr,$$

forms colourless crystals melting at 134—135°.

β-Bromo-α-hydroxydihydroisoeugenol,

$$OH\cdot C_6H_3(OMe)\cdot CH(OH)\cdot CHMeBr,$$

obtained from *iso*eugenol dibromide by the action of aqueous acetone, is a thick liquid which cannot be distilled or made to crystallise; its *methyl ether*, $OH\cdot C_6H_3(OMe)\cdot CH(OMe)\cdot CHMeBr$, is a syrup which yields a crystalline *benzoate* melting at 66—68°; the syrupy *ethyl ether* gives a *benzoate* melting at 72—73°, and is converted by bromine and hydrogen bromide in glacial acetic acid solution into bromo*iso*eugenol dibromide, a fact which indicates its structure.

The foregoing experiments show that whereas the α-bromine atom of *iso*eugenol dibromides is easily replaced by hydroxy- and alkyloxy-groups, the β-bromine atom is only removed by alcoholic sodium methoxide or ethoxide; in dibromoeugenol dibromide,

$$OH\cdot C_6HBr_2(OMe)\cdot CH_2\cdot CHBr\cdot CH_2Br,$$

the β- and γ-bromine atoms have a similar fixity, the substance not being acted on by boiling aqueous acetone or boiling alcohols.

The *acetyl* derivative of bromo*iso*eugenol dibromide forms colourless crystals and melts at 131—132°; that of *iso*eugenol dibromide crystallises in leaflets from alcohol and melts at 125—127°.

W. A. D.

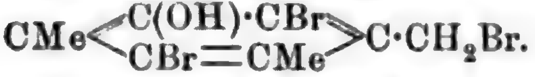
ψ-Phenols from Salicylaldehyde and Salicylic Acid. By KARL AUWERS and L. HUBER (*Ber.*, 1902, 35, 124—131. Compare Stoermer and Behn, Abstr., 1901, i, 726; D.R.-P. 113723, 113512, 114194; and Abstr., 1901, i, 727).—The iodide, $CHO\cdot C_6H_3(OH)\cdot CH_2I$, obtained from salicylaldehyde, formaldehyde, and hydriodic acid, crystallises from a mixture of benzene and light petroleum and melts at 125—126°, not at 87° as given in the German Patent. The *acetate* $CHO\cdot C_6H_3(OH)\cdot CH_2\cdot OAc$, is formed instantaneously when boiling acetic acid solutions of the corresponding iodide, chloride, or bromide and sodium acetate are mixed; it crystallises from glacial acetic acid in thick, colourless needles, melts at 61—62°, and does not behave as a ψ-phenol, inasmuch as it is soluble in dilute alkali and is not acted on by hot dilute acetone. The presence of methyl groups in the benzene nucleus thus appears to be necessary to confer ψ-phenolic properties on acetates of the type dealt with. The *oxime*, $C_8H_9NO_3$, of hydroxymethylsalicylaldehyde crystallises from a mixture of ethyl acetate and light petroleum in yellowish-white needles melting at 120—121°; the *oxime* of the foregoing acetate crystallises from benzene and light petroleum in needles melting at 133—134°. By boiling with acetic anhydride, both oximes are converted into the *diacetyl* derivative, $CN\cdot C_6H_3(OAc)\cdot CH_2\cdot OAc$, of *hydroxymethylsalicylonitrile*, which separates from light petroleum in stout, white crystals and melts at 57—58°.

α-3-Dibromomethylsalicylaldehyde $[CHO:OH:Br:CH_2Br = 1:2:3:5]$, obtained by adding bromine to a glacial acetic acid solution of the preceding acetate melting at 62° and subsequently passing hydrogen bromide into the hot liquid, crystallises from benzene in lustrous needles, melts at 112—113°, and is strongly ψ-phenolic; thus on warming with aqueous acetone it yields *3-bromo-α-hydroxymethylsalicylaldehyde*, which crystallises from benzene in yellowish-white needles and melts at 84—85°. The *acetate*, $CHO\cdot C_6H_2Br(OH)\cdot CH_2\cdot OAc$, of this alcohol, obtained from the bromide by means of sodium acetate, is, however, a true phenol; it forms slender needles and melts at 102°.

α-Chloromethylsalicylic acid [$CO_2H:OH:CH_2Cl = 1:2:5$] readily loses hydrogen chloride when left with methyl alcohol at the ordinary temperature, yielding the *methyl* ether, $CO_2H\cdot C_6H_3(OH)\cdot CH_2\cdot OMe$, which melts at 119°, not at 103° as stated in the German Patent; on passing hydrogen chloride into the methyl alcoholic solution of the ether, the reverse change occurs, chloromethylsalicylic acid being formed.

Methyl methoxymethylsalicylate, $CO_2Me\cdot C_6H_3(OH)\cdot CH_2\cdot OMe$, is obtained by digesting the acid for several hours with methyl alcoholic hydrogen chloride (3—4 per cent.), and is a yellowish oil, soluble in alkalis; on passing hydrogen chloride through its methyl alcoholic solution at the ordinary temperature, it yields *methyl chloromethylsalicylate*, $CO_2Me\cdot C_6H_3(OH)\cdot CH_2Cl$, which crystallises from light petroleum in white needles and melts at 65—66° (compare German Patent). *Methoxymethylsalicylamide*, $NH_2\cdot CO\cdot C_6H_3(OH)\cdot CH_2\cdot OMe$, crystallises from benzene in lustrous needles and melts at 107—108°. W. A. D.

Constitution of the Second ψ-Cumenol Tribromide. By KARL AUWERS and O. ANSELMINO (*Ber.*, 1902, **35**, 131—144. Compare Abstr., 1900, i, 161—162).—The facts dealt with in this paper give confirmatory proof that the dibromohydroxy-ψ-cumyl bromide melting at 128°, obtained by the action of hydrogen bromide on the diacetate of the oxidation product of tribromo-ψ-cumenol, has the structure



$$CMe{<}\begin{matrix}C(OH)\cdot CBr\\ CBr{=}CMe\end{matrix}{>}C\cdot CH_2Br.$$

Dibromo-m-hydroxy-ψ-cumylaniline, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot NHPh$, obtained by digesting the bromide with aniline dissolved in benzene, crystallises from alcohol in small scales and melts at 148—149°; the *diacetyl* derivative crystallises from methyl alcohol in aggregates of rhombic plates, melts at 167—168°, and on warming with dilute alcoholic sodium hydroxide yields the *monoacetyl* derivative, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot NAcPh$, which forms small, rhombic leaflets melting at 216—218°.

m-*Hydroxy-ψ-cumylaniline*, $OH\cdot C_6H_2Me_2\cdot CH_2\cdot NHPh$, obtained by reducing its dibromo-derivative with sodium amalgam, crystallises from a mixture of light petroleum and benzene in concentric aggregates of slender, silky needles melting at 109—110°; the product was not quite pure, but contained 1·63 per cent. of bromine.

o-*Hydroxy-ψ-cumylaniline* [$Me_2:OH:CH_2\cdot NHPh = 1:2:4:5$], obtained by boiling *o*-hydroxy-ψ-cumyl alcohol (Auwers and van de Rovaart, Abstr., 1899, i, 34) with aniline, crystallises from light petroleum containing a few drops of benzene in soft, silky needles and melts at 139—140°; the *diacetyl* derivative crystallises from dilute alcohol in long, white needles melting at 68°, which are hydrated and lose their contained water when heated; the anhydrous substance melts at 85°. The *monoacetyl* derivative separates from light petroleum in nodules and melts at 137—138°.

p-*Hydroxy-ψ-cumylaniline* [$Me_2 : OH : CH_2 \cdot NHPh = 1 : 4 : 3 : 6$] which is not produced when *p*-hydroxy-ψ-cumyl alcohol is heated with aniline either alone or in presence of zinc chloride, is formed, however, in very small quantities when the components are heated in glacial acetic acid solution; it crystallises from alcohol in small prisms, softens at 201—202°, melts at 203—204°, and is also obtained, although in poor yield, by reducing the anil, $OH \cdot C_6H_2Me_2 \cdot CH{:}NPh$, of 2 : 5-dimethyl-4-hydroxybenzaldehyde (Steckhan, *Diss.*, *Heidelberg*, 1900).

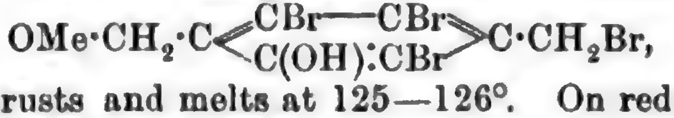
s-*Pentabromo-ψ-cumenol*, $OH \cdot C_6Br_2(CH_2Br)_3$ [$OH : Br_2 = 1 : 2 : 5$], is obtained by heating dibromo-ψ-cumenol with bromine for 8—10 hours at 130°, or pure dibromo-*m*-hydroxy-ψ-cumyl bromide with bromine for 10 hours at 100°; it crystallises from glacial acetic acid in small, dull needles, melts at 174°, and is converted by boiling methyl alcohol into 3 : 6-*dibromo*-2 : 4-*dimethoxydimethyl*-5-*bromomethyl*-1-*phenol* (*dimethyl ether* of *tribromohydroxy-ψ-cumylene*-m-*glycol*),

$$OH \cdot C_6Br_2(CH_2 \cdot OMe)_2 \cdot CH_2Br,$$

which separates from light petroleum in stellate aggregates of needles and melts at 113—114°. On reduction with zinc dust in glacial acetic acid, this yields 3 : 6-*dibromo*-2 : 4-*dimethoxydimethyl*-3-*methyl*-1-*phenol*, which crystallises from water in snow-white needles, melts at 94°, and is converted by hydrogen bromide in boiling glacial acetic acid solution into *dibromohydroxy-ψ-cumylene dibromide*,

$$OH \cdot C_6Br_2Me(CH_2Br)_2 \; [OH : Br_2 : Me : (CH_2Br)_2 = 1 : 2 : 5 : 3 : 4 : 6];$$

the latter crystallises in rosettes of lustrous needles, and melts at 149—150°.

s-Pentabromo-*p*-xylenol (tribromohydroxy-*p*-xylylene dibromide, m. p. 184°; Abstr., 1900, i, 160) is obtained by heating tribromo-*p*-xylenol with bromine for 5—6 hours at 130°, and is easily transformed by boiling methyl alcohol into the *methyl ether* of *tribromohydroxy*-p-*xylylene bromohydrin*,  $OMe \cdot CH_2 \cdot C \begin{matrix} \nearrow CBr\text{—}CBr \searrow \\ \searrow C(OH){:}CBr \nearrow \end{matrix} C \cdot CH_2Br$, which crystallises in compact crusts and melts at 125—126°. On reduction, it yields the *methyl ether* of *tribromo-o-hydroxy*-p-*xylyl alcohol*,

$$OH \cdot C_6MeBr_3 \cdot CH_2 \cdot OMe,$$

which crystallises from dilute methyl alcohol in small needles, melts at 62—63°, and on treatment with hydrogen bromide in hot glacial acetic acid solution gives *tribromo*-o *hydroxy*-p-*xylyl bromide*,

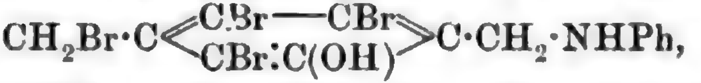
$$OH \cdot C_6MeBr_3 \cdot CH_2Br,$$

crystallising from light petroleum in short, flat needles and melting at 117°. W. A. D.

Derivatives of Phenol Bromides. By O. Anselmino (*Ber.*, 1902, **35**, 144—150).—3 : 6-Dibromo-5-hydroxy-ψ-cumyl bromide, when treated with pyridine, yields *dibromohydroxy-ψ-cumylpyridine hydrobromide*, which crystallises in silky, hair-like needles melting at 237—238°.

When treated with potassium iodide, it gives *dibromohydroxy-ψ-cumyl iodide*, which crystallises in short compact needles, melts at 153—154°, and forms an *acetyl* derivative crystallising in needles and melting at 124—125°. The corresponding *chloride*, obtained by treating the diacetate of the alcohol (Abstr., 1900, i, 162) with hydrogen chloride, crystallises in white needles, melts at 99—100°, is easily soluble in most solvents, and forms an *acetyl* derivative which crystallises in needles melting at 94—95°.

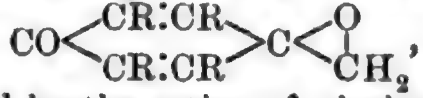
2 : 4 : 6-*Tribromo-5-hydroxy-xylylene dibromide*, obtained by the action of bromine on the tribromohydroxy-xylene, crystallises from alcohol in small, felted needles, melts at 201°, is soluble in alkalis and not decomposed by boiling with acetone and water, being a normal phenol. On the other hand, dibromo-ψ-cumenol tribromide, when boiled with acetone and water, yields the *bromide* of *dibromohydroxy-ψ-cumylene*-m-*glycol*, which crystallises from ethyl acetate in compact prisms and melts and decomposes at 153°.

Tribromo-*p*-xylenol dibromide yields, when treated with aqueous acetone, the corresponding *bromohydrin* which crystallises in small needles melting at 142—143°; when treated with aniline, the *compound*,  $CH_2Br\cdot C{<}\substack{CBr—CBr\\ CBr:C(OH)}{>}C\cdot CH_2\cdot NHPh$, which crystallises in silky needles, and softens and decomposes without melting at 138—140°, and, when treated with *o*-toluidine, the corresponding *compound*, which is an orange-red, crystalline powder, and softens and decomposes at 120—125°.

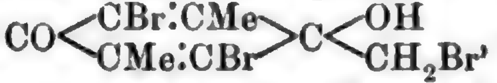
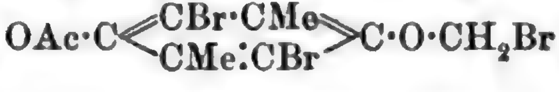
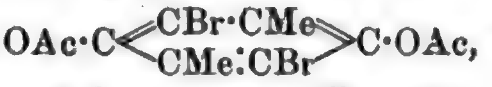
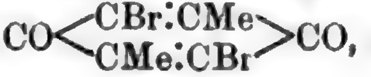
The *ethyl* ether of dibromo-ψ-cumenol crystallises in fan-shaped clusters of needles melting at 55—56°; the *methyl* ether of tetrabromo-*o*-cresol in needles melting at 140·5°, and the *methyl* ether of tetrabromo-*m*-cresol in small needles melting at 145—146°, all three ethers being unattacked by moist bromine. R. H. P.

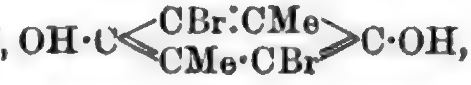
Constitution of Oxidation Products from Halogenated ψ-Phenols.

By **Karl Auwers** and **A. Sigel** (*Ber.*, 1902, **35**, 425—442).—Confirmation is given of Zincke's formula,



$$CO{<}\substack{CR:CR\\ CR:CR}{>}C{<}\substack{O\\ |\\ CH_2},$$

for the oxides obtained by the action of alcoholic potash on the halogenated ψ-quinols such as that,  $CO{<}\substack{CBr:CMe\\ CMe:CBr}{>}C{<}\substack{OH\\ CH_2Br}$, which is formed by oxidising tribromo-ψ-cumol. Addition of acetyl bromide or acetic anhydride to the oxides takes place, however, at the para-positions, giving compounds such as  $OAc\cdot C{<}\substack{CBr\cdot CMe\\ CMe:CBr}{>}C\cdot O\cdot CH_2Br$ and  $OAc\cdot C{<}\substack{CBr\cdot CMe\\ CMe:CBr}{>}C\cdot OAc$, which have already been described, although formulated differently. Sulphuric acid causes this oxide, as well as the two additive products, to decompose into dibromo-*p*-xyloquinone,  $CO{<}\substack{CBr:CMe\\ CMe:CBr}{>}CO$, and formaldehyde.

*Dibromo-*p*-xyloquinol*,  $OH\cdot C{<}\substack{CBr:CMe\\ CMe\cdot CBr}{>}C\cdot OH$, forms white, glisten-

ing flakes, crystallises from acetic acid, and melts at 174—175°; the *diacetate* crystallises from acetic acid in small, white prisms and melts at 212—213°; the *monoacetyl* derivative is best prepared by hydrolysing acetylacetonyldibromo-*p*-xyloquinol, and its formation affords proof of the correctness of the formula now assigned to the latter; it forms stout, white or yellowish, glistening crystals, melts at 139—140°, crystallises from toluene, is slowly hydrolysed in alkaline solution to dibromoxyloquinol, and is converted by acetic anhydride into the diacetate; the *acetyl-benzoyl* derivative crystallises from methyl alcohol in white or yellowish prisms, melts at 162—163°, and is stable towards cold aqueous alkalis but quickly hydrolysed on heating.

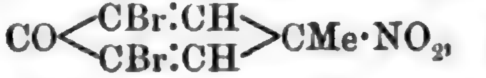
Bromomethyldibromoxyloquinol iso*butyrate*,

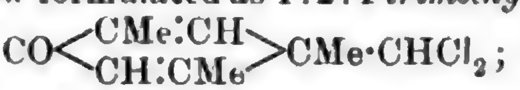
$$COPr^{\beta}\cdot O\cdot C_6Me_2Br_2\cdot O\cdot CH_2Br,$$

from *iso*butyryl bromide and the oxide, crystallises from methyl alcohol in white, silky needles and melts at 88°. The *acetonyl* iso*butyrate*, $COPr^{\beta}\cdot O\cdot C_6Me_2Br_2\cdot O\cdot CH_2Ac$, prepared by the action of acetic acid and sodium acetate on the preceding compound, crystallises from light petroleum in white needles and melts at 55°; it is hydrolysed by methyl alcoholic sodium hydroxide to *dibromoxyloquinol monoisobutyrate*, $OH\cdot C_6Me_2Br_2\cdot O\cdot COPr^{\beta}$, which crystallises from light petroleum in minute, snow-white, glistening prisms, and melts at 119°; the *acetate*, $OAc\cdot C_6Me_2Br_2\cdot CO_2Pr^{\beta}$, of the latter, which can also be prepared by the action of sodium *iso*butyrate on the acetyl bromide derivative of the original oxide, forms minute, white needles, and melts at 119°; its formation by these two methods affords evidence that the additive compounds of the oxide are derived from the quinol and not from the ψ-quinol.

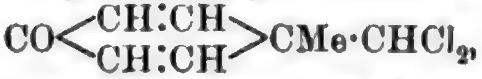
The *methylene* ether, $CH_2(O\cdot C_6Me_2Br_2\cdot OAc)_2$, of monoacetyldibromoxyloquinol, prepared by the action of methylene iodide on the sodium salt, forms white, thread-like needles, melts at 202°, and, like the methylene ether of tribromophenol, is only slowly hydrolysed by hot alkalis; it can also be prepared by the action on the sodium salt of the acetyl bromide derivative of the oxide, and therefore affords a direct proof of the constitution of the latter. T. M. L.

ψ-Quinols and Cyclic Nitroketones. By KARL AUWERS (*Ber.*, 1902, **35**, 443—455).—A theoretical paper containing a summary of the work of Zincke, Bamberger, and the author on the ψ-quinols. The last part of the paper deals with the similarly constituted nitroketones (compare the following abstract). T. M. L.

Nitro-ketone and ψ-Quinol of Dibromo-*p*-cresol. By KARL AUWERS (*Ber.*, 1902, **35**, 455—464).—3 : 5-*Dibromo*-1-*nitro*-4-*keto-dihydrotoluene*,  $CO<\begin{matrix}CBr\!:\!CH\\CBr\!:\!CH\end{matrix}>CMe\cdot NO_2$, prepared by the action of nitric acid on dibromo-*p*-cresol, is a white, sandy compound, melts and decomposes at 62—65°, and rapidly becomes yellow and then brown on exposure to air and light. When left under water or aqueous alkalis or ammonium sulphide solution, or when moistened with alcohol and exposed to air, it is converted into 3-*bromo-5-nitro-p-cresol*, $\mathrm{OH{\cdot}C}<\substack{\mathrm{CBr—CH}\\ \mathrm{C(NO_2){:}CH}}>\mathrm{CMe}$, which crystallises from light petroleum and melts at 69°; its *acetyl* derivative crystallises from dilute acetic acid in glistening needles and melts at 110—111°. 3 : 5-*Dibromo*-1-*methyl*-4-*ψ-quinol*, $\mathrm{CO}<\substack{\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CH}}>\mathrm{CMe{\cdot}OH}$, prepared by adding the nitro-ketone to acetic acid heated to 40—50°, or by leaving it exposed to the air in a desiccator, or by the action of nitrous fumes on a solution in acetic acid of dibromo-*p*-cresol, forms brilliant, diamond-like prisms and tablets belonging to the monoclinic system, crystallises from benzene, and melts at 134·5°. The isomeric quinol melts at 149—150° and not at 117° (Claus and Hirsch, Abstr., 1889, 389). Dibromo-*p*-hydroxybenzyl bromide, $OH{\cdot}C_6H_2Br_2{\cdot}CH_2Br$, is formed as a bye-product in the preparation of the ψ-quinol from dibromo-*p*-cresol. The *acetyl* derivative of the ψ-quinol crystallises from dilute acetic acid in minute needles, from methyl alcohol in rhombic crystals, and melts at 116—117°. The *benzoyl* derivative crystallises from amyl alcohol in microscopic crystals, melts at 204°, and dissolves readily in alcohol and in acetic acid. The ψ-quinol and its esters are readily reduced to dibromo-*p*-cresol, whilst hydrogen bromide or phosphorus pentabromide gives tribromo-*p*-cresol. Tribromo-*p*-cresol melts at 96° (Wagner, *Diss. Marburg*, 1899, gives 102°) and its acetate at 72—73° (Wagner gives 77°); tetrabromo-*p*-cresol melts at 193—194° (Wagner gives 196°) and yields a ψ-quinol, which is reduced again to the cresol by hydrogen bromide. T. M. L.

Cyclic Ketones from Chloroform and Phenols. By KARL AUWERS and F. WINTERNITZ (*Ber.*, 1902, **35**, 465—471).—The chlorinated product formed on attempting to prepare hydroxydimethylbenzaldehyde by the action of chloroform and alkali on ψ-cumenol (Abstr., 1885, 380; 1886, 143) is shown to be a ketone constituted similarly to the ψ-quinols, and is now formulated as 1 : 2 : 4-*trimethyl*-2-*dichloromethyl*-5-*ketodihydrobenzene*,  $\mathrm{CO}<\substack{\mathrm{CMe{:}CH}\\ \mathrm{CH{:}CMe}}>\mathrm{CMe{\cdot}CHCl_2}$; it is reduced by zinc dust and acetic acid to methylene chloride and ψ-cumenol. The *dibromo*-derivative, $\mathrm{CO}<\substack{\mathrm{CMe{:}CBr}\\ \mathrm{CBr{:}CMe}}>\mathrm{CMe{\cdot}CHCl_2}$, prepared in a similar way from dibromo-ψ-cumenol, crystallises from light petroleum in stout prisms and melts at 99—100°.

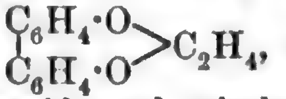
1-*Methyl*-1-*dichloromethyl*-4-*ketodihydrobenzene*,


$$\mathrm{CO}<\substack{\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}}>\mathrm{CMe{\cdot}CHCl_2},$$

from *p*-cresol and chloroform, crystallises from light petroleum in minute needles and melts at 55°. 1 : 3-*Dimethyl*-1-*dichloromethyl*-4-*ketodihydrobenzene*, $\mathrm{CO}<\substack{\mathrm{CMe{:}CH}\\ \mathrm{CH{=}CH}}>\mathrm{CMe{\cdot}CHCl_2}$, from *as-m*-xylenol, separates from light petroleum in stout crystals and melts at 56°.

o-Cresol and *p*-xylenol, which do not contain a methyl group in the para-position to the hydroxyl, behave in the normal way and give only the aldehyde; the aldehyde also appears as a bye-product in the case of *p*-cresol and *m*-xylenol. T. M. L.

2 : 2′-**Diphenol.** By **Otto Diels** and **Arthur Bibergeil** (*Ber.*, 1902, **35**, 302—313).—2 : 2′-Diphenol sinters at 103°, melts at 109° (corr.), and boils at 325—326° (corr.) under 755 mm. pressure; when dissolved in hot water, it yields a crystalline, efflorescent *hydrate* melting at 71—73°. The dimethyl ether formed by its methylation is identical with that obtained by Jannasch and Kölitz (Abstr., 1898, i, 190) from *o*-iodoanisole and sodium; the *ethylene ether*,



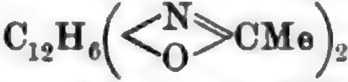
$\begin{matrix}C_6H_4\cdot O \\ | \\ C_6H_4\cdot O\end{matrix}\!>\!C_2H_4$,

obtained by heating the diphenol with potassium hydroxide and ethylene bromide for 15 hours at 140—150°, crystallises from alcohol, on diluting with water, in lustrous, spindle-shaped needles and melts at 98° (corr.). The *urethane*, $C_{12}H_8(O\cdot CO\cdot NHPh)_2$, obtained by heating the diphenol with phenylcarbimide for 15 hours at 100°, crystallises from dilute alcohol in beautiful needles and melts at 144—145° (corr.).

Dibromo-2 : 2′-*diphenol*, obtained by the action of bromine in chloroform solution at the ordinary temperature, melts at 188—189° (corr.); the *tetrabromo*-derivative, formed on brominating the diphenol in hot glacial acetic acid, crystallises from alcohol in silky needles with $1H_2O$, and melts at 204—205° (corr.). The action of chlorine on 2 : 2′-diphenol is so energetic that only the *tetrachloro*-derivative could be obtained; this crystallises from a mixture of benzene and light petroleum in needles and melts at 178° (corr.).

3 : 3′-*Dinitro*-2 : 2′-*diphenol*, obtained by nitrating the diphenol in glacial acetic acid solution at 0°, is purified by crystallising the product from absolute alcohol, when the isomeric dinitro-compound (*infra*) remains in solution; it crystallises in yellowish-brown needles, melts at 189—190° (corr.), and on reduction with tin and hydrochloric acid yields 3 : 3′-*diamino*-2 : 2′-*diphenol*, which forms colourless needles, darkens at 190°, and melts and decomposes at 227° (corr.); the *dihydrochloride*, with $2H_2O$, forms colourless crystals.

Tetra-acetyl-3 : 3′-*diamino*-2 : 2′-*diphenol* crystallises from methyl alcohol, melts at 242° (corr.), and on distillation yields *bis*-1-*methylbenzoxazole*,



$C_{12}H_6\left(<\begin{matrix}N\\O\end{matrix}>CMe\right)_2$,

which separates from alcohol in small plates, and melts at 150° (corr.); the formation of this shows the structure of the foregoing compounds.

5 : 5′-*Dinitro*-2 : 2′-*diphenol* differs from its congener in being more soluble in boiling water and in alcohol; it crystallises in yellowish-brown needles, melts and decomposes at 240—250°, and on reduction yields 5 : 5′-*diamino*-2 : 2′-*diphenol*, which forms slightly violet needles, melts at 246° (corr.), and cannot be recrystallised owing to its sparing solubility in all solvents; the *hydrochloride* forms greyish, cubical aggregates of needles, and is easily soluble in water.

3 : 3′ : 5 : 5′-*Tetranitro*-2 : 2′-*diphenol*, obtained by nitrating the diphenol at 0° in glacial acetic acid and subsequently warming on the water-bath, crystallises best on slightly diluting its glacial acetic acid solution; it forms bright yellow crystals, melts at 248—249° (corr.), and on reduction yields a *tetra-amino*-compound which crystallises in small

needles and rapidly decomposes in the air; the *tetrahydrochloride*, forming small, grey or violet crystals, was analysed.

2 : 2'-*Dihydroxydiphenyl*-5 : 5'-*disulphonic acid* is formed on dissolving the diphenol in concentrated sulphuric acid at 50—60°; the *lead* salt, with $5H_2O$, forms large, lustrous crystals, and the *sodium* salt, which is very soluble in water, crystallises in plates. On nitration in aqueous solution, the free acid yields 5 : 5'-dinitro-2 : 2'-diphenol, a fact indicating its structure.

On sulphonation at 150°, the 2 : 2'-diphenol yields 2 : 2'-*dihydroxydiphenyl*-3 : 3' : 5 : 5'-*tetrasulphonic acid*; the *lead* salt,

$$C_{12}H_{14}O_{14}S_4Pb_3,10H_2O,$$

which is sparingly soluble in water, forms microscopic needles.

W. A. D.

Extraction of Boletol. By GABRIEL BERTRAND (*Compt. rend.*, 1902, **134**, 124—126).—In order to extract boletol (this vol., ii, 166) from *Boletus*, the fungus must be freshly gathered, cut up into thin slices, and boiled for not less than half-an-hour with five times its weight of alcohol of 95°. The boletol is precipitated by means of lead acetate, liberated from the precipitate by the action of hydrochloric acid, and extracted with ether. Part of the boletol remains in the lead acetate precipitate, and if this is treated with ether, fats and boletol are dissolved together, and the boletol can be separated by treatment with water. The fats in the fungus have a marked power of dissolving boletol, and this fact can be utilised in isolating the substance. Boletol crystallises in slender needles, only slightly soluble in cold water, ether, or alcohol, but readily so in hot ether or alcohol, from which it does not separate on cooling. C. H. B.

Derivatives of Benzoin containing Sulphur. By THEODOR POSNER (*Ber.*, 1902, **35**, 506—510).—The substance obtained by the condensation of benzoin and ethyl hydrosulphide (Abstr., 1901, i, 15) is diethylthiolstilbene. Analogous compounds have been prepared by condensation with other mercaptans. *Dibenzylthiolstilbene*,

$$C_7H_7{\cdot}S{\cdot}CPh{:}CPh{\cdot}S{\cdot}C_7H_7,$$

crystallises in needles melting at 174—175°, *diamylthiolstilbene* in long needles melting at 76—77°, and *diphenylthiolstilbene* in long needles, which sinter at 144° and melt at 160—162°. R. H. P.

Disulphones. VIII. Mercaptoles and Sulphones from Diketones. By THEODOR POSNER (*Ber.*, 1902, **35**, 493—505).—An elaboration of the fourth part (Abstr., 1901, i, 14). The action of phenyl, amyl, benzyl, and ethyl mercaptans on various diketones is compared. The methods employed are similar to those previously described (*loc. cit.*).

α-Diketones.—$\beta\beta\gamma\gamma$-*Tetrabenzylthiolbutane* (*diacetyldibenzylmercaptole*), $CMe(S{\cdot}C_7H_7)_2.CMe(S{\cdot}C_7H_7)_2$, crystallises in short needles, melting at 164—165° *, and when oxidised yields the corresponding *sulphone*, which crystallises in clusters of needles and melts at 195—196°.

$\beta\beta$-*Diamylsulphonebutane*-γ-*one* (*diacetyldiamylsulphone*) is a light yellow, clear oil. Phenyl hydrosulphide does not condense with diacetyl or acetylpropionyl. *ββ-Dibenzylsulphonepentane-γ-one* is an uncrystallisable substance, which is precipitated when its alcoholic solution is cooled. *ββ-Diamylthiolpentane-3-one* (*acetylpropionylmonoamylmercaptole*) and the corresponding *sulphone* are oils.

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* All melting points are corrected.

αβ-Diphenyl-αα-dibenzylthiolethane-β-al (*benzilmonobenzylmercaptole*) crystallises in long, rhombic needles, melts at 101—103°, but does not yield a disulphone. *αβ-Diphenyl-αα-diphenylthiolethane-2-al*,

$$CPh(SPh)_2\cdot COPh,$$

crystallises in long needles, melts at 138°, and does not yield a disulphone.

β-Diketones.—*ββδδ-Tetrabenzylthiolpentane* (*acetylacetonedibenzylmercaptole*), $CMe(SC_7H_7)_2\cdot CH_2\cdot CMe(SC_7H_7)_2$, crystallises in clusters of long needles, melts at 65—66°, and, when oxidised, yields *ββ-dibenzylsulphonepentane-β-one*, which crystallises in white leaflets and melts at 137—138°.

ββ-Diamylsulphonepentane-δ-one is a light yellow, viscous oil. *ββ-Dibenzylsulphone-γ-methylpentane-δ-one*,

$$CMe(SO_2C_7H_7)_2\cdot CHMe\cdot COMe,$$

forms small, laminated crystals and melts at 149—151°. *ββ-Diamylsulphone-γ-methylpentane-δ-one* and *ββ-diphenylthiol-γ-methylpentane-δ-one* are oils, the latter yielding no sulphone. *α-Phenyl-γγ-dibenzylsulphonebutane-α-al* (*benzoylacetonedibenzylsulphone*) melts at 70—76°; *α-phenyl-γγ-diamylthiolbutane-α-al* and the corresponding *sulphone* are oils. The *mercaptole*, obtained by the condensation of benzoylacetone and phenyl hydrosulphide, does not yield a sulphone.

γ-Diketones.—*ββεε-Tetrabenzylthiolhexane* (*acetonylacetonedibenzylmercaptole*), $CMe(SC_7H_7)_2\cdot C_2H_4\cdot CMe(SC_7H_7)_2$, crystallises in long needles, melts at 98—99°, and when oxidised yields the corresponding *sulphone*, which sinters at 176° and melts and decomposes at 222—227°. *ββεε-Tetraphenythiolhexane* is a colourless oil, but the corresponding *sulphone* crystallises in long needles melting at 139—140°. *ββεε-Tetraphenylthiolhexane* crystallises in small, lustrous needles, melts at 137—138°, and, in contradistinction to the mercaptoles from α- and β-diketones, yields a *sulphone*, which is a crystalline powder, melting and decomposing at 244°. *β-Methyl-γγζζ-tetrabenzylthiolheptane* (*dimethylacetonylacetonebenzylmercaptole*),

$$CHMe_2\cdot C(SC_7H_7)_2\cdot C_2H_4\cdot C(SC_7H_7)_2Me,$$

is a colourless oil, but the corresponding *sulphone* crystallises in laminæ and melts at 202—203°. The condensation product of dimethylacetonylacetone and phenyl hydrosulphide could not be purified, but when oxidised yielded *β-methyl-ζζ-diphenylsulphoneheptane-γ-one*, which is a crystalline powder melting at 117—118°.

R. H. P.

The Comparison of Sulphoxides with Ketones. By J. A. Smythe (*Proc. Univ. Durham*, 1901, **2**, 9—10).—The analogy of benzyl sulphoxide to the ketones is chiefly structural, the sulphoxides being much more stable compounds than the ketones. Reduction of the sulphoxide does not lead to compounds analogous to the secondary alcohols or pinacones; alkaline reducing agents are without action on the sulphoxide, whilst acid reducing agents convert it into benzyl sulphide. Phenylhydrazine and hydroxylamine are without action on the sulphoxide. The sulphoxide condenses with benzyl mercaptan, forming a crystalline compound melting at 70°. When acted on by phosphorus pentachloride, dibenzyl disulphide is formed. The author also shows that benzyl sulphide and hypochlorous acid yield benzylsulphonic chloride, $C_6H_5 \cdot CH_2 \cdot SO_2Cl$, melting at 91—92°. A. F.

Characterisation of "Pseudo-acids" by the Abnormal Relationship of their Affinity Constants and Hydrolysis of their Salts. By ARTHUR HANTZSCH and AD. BARTH (*Ber.*, 1902, **35**, 210—226. Compare Abstr., 1899, i, 399).—The usual relationship between the affinity constant of an acid and the hydrolysis of its sodium salt is represented by the formula $x^2/(1-x)v = a^2/k$ where x is the percentage of sodium salt hydrolysed, v is the dilution in litres, a the dissociation factor of water, according to Van't Hoff, and k the affinity constant of the acid. This relationship has been shown by Walker (Abstr., 1900, ii, 268) to hold good for even very feeble acids.

The following conclusion has been previously drawn, namely, that when a non-conducting hydrogen compound yields an alkali salt which is not hydrolysed, or only very slightly so, then the alkali salt must have a different constitution from the original hydrogen compound, or abnormal neutralisation phenomena characterise a hydrogen compound as a pseudo-acid. As a rule, this phenomenon is rarely met with, as most pseudo-acids are electrolytes to a certain extent, and the alkali salts of these acids are hydrolysed to a certain extent.

The authors mention a second criterion by means of which pseudo-acids may be detected, namely, when the affinity constant and degree of hydrolysis do not agree with the above equation; in other words, when $x^2/(1-x)v < a^2/k$. The hydrolysis of the sodium salts may be determined by Shields' method (Abstr., 1893, ii, 448) or by Farmer's method (Trans., 1901, **79**, 863).

When the amount of hydrolysis is too small to estimate, the following argument is employed. A salt with a neutral or practically neutral action must correspond with a true acid, the ionisation of which must be at least as great as that of acetic acid ($K = 180000 \times 10^{-10}$). If the affinity constant of the acid is much below that of acetic, then the hydrogen compound must be a pseudo-acid. As phenol ($K = 1 \cdot 3 \times 10^{-10}$) when strongly diluted has a distinctly acid action, all hydrogen compounds which are neutral are less strongly acid and must have a smaller constant; they must therefore, if they are true acids, yield sodium salts which are hydrolysed to a greater extent than sodium phenoxide (5·4 per cent. at v_{32} and 25°). If the extent of hydrolysis is found to be much smaller, then the original hydrogen compounds must be pseudo-acids.

By this means, acetic, carbonic, boric, and hydrocyanic acids, hydrogen sulphide, and phenol have proved to be true acids.

*iso*Nitrosophenylmethylpyrazolone, *iso*nitrosomethylpyrazolone, *iso*nitrosodiketohydrindene, *o*-toluquinoneoxime, *p*-quinoneoxime, *iso*nitrosothiohydantoin, ethylnitrolic acid, isatinoxime, ethylisatinoxime, and *iso*nitrosoacetone have been characterised as pseudo-acids.

J. J. S.

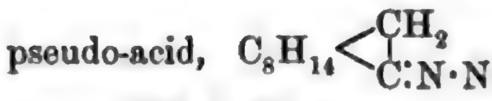
Characterisation of "Pseudo-acids" by the Ammonia Reaction.

By Arthur Hantzsch and Fritz E. Dollfus (*Ber.*, 1902, **35**, 226—265. Compare Abstr., 1899, i, 399).—The authors have employed the ammonia reaction previously described in order to determine whether various hydrogen compounds which give rise to salts are true acids or pseudo-acids. The method is readily applicable when the following conditions are fulfilled: (1) the compound yields an ammonium salt in ionising media, (2) the ammonium salt is insoluble in non-ionising liquids, (3) the compound yields no precipitate of the ammonium salt with dry ammonia in the non-ionising liquids. As a rule, it is merely necessary to see whether the hydrogen compound yields a precipitate of the ammonium salt in ethereal, but not in benzene, light petroleum, or chloroform solution; if so, the compound must be a pseudo-acid provided the ammonium salt is insoluble in the media named.

A modified apparatus is described by means of which the amount of hydrogen compound transformed into ammonium salt may be estimated.

Under these conditions even the feeblest true acids, for example, phenols and oximes, combine with ammonia. The method possesses advantages over the electrochemical method, since it can be employed in non-ionising media, and thus the constitution of the undissociated hydrogen compounds determined. It is of special use in distinguishing between groups of isomeric and tautomeric substances and for detecting ionising isomerism. The conclusion that all compounds which combine directly with ammonia in benzene solution are true acids cannot be drawn, as a pseudo-acid may undergo isomerisation in the benzene solution under the influence of the ammonia. All enolic substances yield ammonium salts in non-ionising media, for example, the enolic forms of dibenzoylacetone, ethyl diacetylsuccinate, ethyl benzylideneacetoacetate, ethyl diketotetrahydropyridinecarboxylate, and oxymethylenecamphor. When both forms are sufficiently stable, the ammonia reaction serves as a simple method for the quantitative separation of the two isomeric (tautomeric) forms. The so-called ketopentamethylene derivatives consist almost entirely of the enolic forms, whereas ketohexamethylene compounds consist mainly of the ketonic forms; for example, ethyl diketohydrindenedicarboxylate is really ethyl hydroxyindonecarboxylate and ethyl phloroglucinoltricarboxylate, ethyl triketohexamethylenetricarboxylate. Ethyl acetoacetate and ethyl benzoylacetate react as ketones, ethyl oxalylacetate as an enol, and triphenylvinyl alcohol is probably triphenylethanone.

All acid amides are pseudo-acids; they possess in the solid and non-dissociated state the constitution R·CO·NHX, whereas their alkali salts have the constitution R·C(OM):NX. The true acids, the *iso*amides, R·C(OH):NX, have so far not been obtained in the solid state. The tendency of these pseudo-acids to pass over into salts or ions of the true acids increases with the negative nature of the X group (Br, Cl, CN, NO_2).

Nitroamines, R·NH·NO_2, are also pseudo-acids and show a great tendency to undergo ionising isomerism. With camphenylnitroamine, the isomeric true acid, $C_8H_{14}<\begin{matrix}CH\\ \Vert\\ C\cdot N:NO\cdot OH\end{matrix}$, has been isolated and melts at 39°; the pseudo-acid,  $C_8H_{14}<\begin{matrix}CH_2\\ | \\ C{:}N\cdot NO_2\end{matrix}$, melts between 65° and 70° (Angeli, Abstr., 1897, i, 87).

Most α-oximinoketones, $R_1\cdot CO\cdot C({:}NOH)R_2$, react as hydroxylic compounds, a few, for example, *syn*.benziloxime, isatoxime, and quinoneoxime, react as pseudo-acids.

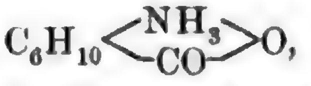
Certain pseudo-acids (nitroamines) form additive products with ammonia, which become transformed into the true ammonium salts. These additive products probably correspond with the abnormal hydrates, which may be isolated from certain pseudo-acids.

The metallic derivatives of β-ketonic esters form unstable additive compounds with ammonia. J. J. S.

Reduction of *m*-Aminobenzoic Acid. By RUDOLPH BAUER and ALFRED EINHORN (*Annalen*, 1901, **319**, 324—344. Compare Einhorn and Meyenberg, Abstr., 1894, i, 591).—*m*-Aminobenzoic acid when reduced with sodium and amyl alcohol gives rise to *m-isoamylaminobenzoic acid*, iso*amylaminohexahydrobenzoic acid*, *aminohexahydrobenzoic acid*, m-*hydroxy*iso*amylbenzoic acid*, *m*-hydroxyhexahydrobenzoic acid, and hexahydrobenzoic acid.

The *hydrochloride* of *m-iso*amylaminobenzoic acid separates, on acidifying the product of reaction with hydrochloric acid, in lustrous crystals and melts at 257°; it dissolves but sparingly in alcohol, and is insoluble in ether or ethyl acetate. The acid $C_5H_{11}\cdot NH\cdot C_6H_4\cdot CO_2H$ is a solid substance, softening at 47° and melting at 54°. Its *nitroso*-derivative, $NO\cdot N(C_5H_{11})\cdot C_6H_4\cdot CO_2H$, crystallises from benzene in yellowish-white leaflets melting at 131—132°, and giving the Liebermann reaction.

The other two amino-acids are isolated from the products of reduction in the form of their ethyl esters, the latter being prepared by boiling the crude hydrochlorides with alcohol saturated with hydrogen chloride. *Ethyl* m-*aminohexahydrobenzoate*, $NH_2\cdot C_6H_{10}\cdot CO_2Et$, a colourless, pungent oil boiling at 123° under 11 mm. pressure, exhibits little tendency to form crystalline salts with acids; its *platinichloride*, an orange-coloured, granular, crystalline mass, decomposes at 233°. The *benzoyl* derivative and the *carbamide* are crystalline substances, melting at 111° and 141° respectively. The *chloroacetyl* derivative and *phenylthiocarbamide* crystallise in colourless needles, and melt respectively at 115° and 149°.

m-*Aminohexahydrobenzoic acid*,  $C_6H_{10}<\begin{matrix}NH_3\\ CO\end{matrix}>O$, resulting from the hydrolysis of the ethyl ester with boiling water, separates from this solvent on the addition of alcohol and acetone in colourless crystals melting at 268—269°; it sublimes in a vacuum and is neutral to litmus. The *hydrochloride*, $CO_2H\cdot C_6H_{10}\cdot NH_2,HCl$, crystallises from alcohol and ether in white leaflets and melts at 156°; the *platinichloride* forms orange-coloured prisms decomposing at 239°. *m*-Hydroxyhexahydrobenzoic acid, produced by treating ethyl *m*-aminohexahydrobenzoate with nitrous acid and boiling the product with water, melts at 125·5°, the melting point of this substance, as determined by Coblitz and Einhorn, being 132°.

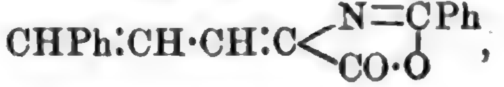
Ethyl m-isoamylaminohexahydrobenzoate, $C_5H_{11}\cdot NH\cdot C_6H_{10}\cdot CO_2Et$, obtained from the reduction products of *m*-aminobenzoic acid or m-*iso*-amylaminobenzoic acid in the manner indicated, is a colourless oil boiling at 153—155° under 11 mm. pressure; its *nitroso*-compound is a greenish-yellow oil, and its *aurichloride* forms yellow crystals melting at 131°.

The hydroxy-acids formed in the reduction of *m*-aminobenzoic acid are separated by fractional precipitation with hydrochloric acid from their solution in sodium carbonate. m-*Hydroxy*-o-iso*amylbenzoic acid*, $C_5H_{11}\cdot C_6H_3(OH)\cdot CO_2H$, the first fraction obtained in this manner, separates from benzene in colourless, lustrous crystals melting at 177°. *Ethyl* m-*hydroxy*-o-iso*amylbenzoate*, $C_5H_{11}\cdot C_6H_3(OH)\cdot CO_2Et$, produced by alkylating the acid with boiling alcohol saturated with hydrogen chloride, separates from light petroleum in silky, filiform crystals and melts at 75°; it dissolves in sodium hydroxide solution, and is reprecipitated by carbon dioxide.

From the second fraction obtained by precipitation with hydrochloric acid, hexahydrobenzoic acid and *m*-hydroxyhexahydrobenzoic acid were isolated, the latter in the form of its *ethyl* salt; this ester boils at 140—150° under 11 mm. pressure, and yields a yellow *sodium* derivative. The reduction of *m*-aminobenzoic acid with sodium in ethyl alcohol leads to the formation of (1) aminohexahydrobenzoic acid, which is isolated in the form of its ethyl salt, boiling at 123° under 11 mm. pressure, and (2) m-*hydroxy*-o-*ethylbenzoic acid*, $OH\cdot C_6H_3Et\cdot CO_2H$, which crystallises from water in colourless, silky needles melting at 172°. The hydroxy-acid is readily soluble in the ordinary solvents; its *methyl* and *ethyl* esters are readily prepared from the corresponding alcohol and hydrogen chloride, the former crystallises in colourless leaflets melting at 71°, and the latter separates in filiform crystals which melt at 96°. The esters dissolve in solutions of sodium hydroxide, and are reprecipitated by carbon dioxide.

m-*Acetoxy*-o-*ethylbenzoic acid*, $OAc_2\cdot C_6H_3Et\cdot CO_2H$, produced by adding concentrated sulphuric acid to an acetic anhydride solution of *m*-hydroxy-*o*-ethylbenzoic acid, crystallises from alcohol in colourless needles and melts at 145°. The corresponding *benzoyl* derivative, prepared by the Schotten-Baumann reaction, crystallises from dilute alcohol in colourless leaflets melting at 177°. These acyl derivatives are soluble in sodium carbonate solution. G. T. M.

Synthesis of α-Naphthoic Acid and Naphthalene. By EMIL ERLENMEYER, jun., and J. KUNLIN (*Ber.*, 1902, **35**, 384—386. Compare Abstr., 1893, i, 580; 1899, i, 759).—Cinnamaldehyde and hippuric acid condense, forming a yellow anhydride,



$$\mathrm{CHPh{:}CH\cdot CH{:}C}{<}\begin{matrix}\mathrm{N{=}CPh}\\ \mathrm{CO\cdot O}\end{matrix},$$

which, with alkalis, yields a yellow acid,

$$\mathrm{CHPh{:}CH\cdot CH{:}C(CO_2H)\cdot NH\cdot COPh}.$$

The latter is decomposed only slowly by alkalis, with the production of ammonia, phenylacetaldehyde, &c. When heated with excess of concentrated hydrochloric acid under pressure at 110—120° for 18 hours, a mixture of naphthalene, α-naphthoic acid, and benzoic acid is formed. The yellow acid first decomposes into benzoic acid, ammonia, and the *a*-ketonic acid, $CHPh{:}CH{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, which then condenses with formation of the naphthalene ring. K. J. P. O.

Tolyl Purpurates. By WALTHER BORSCHE and U. LOCATELLI (*Ber.*, 1902, **35**, 569—576. Compare Abstr., 1900, i, 645).—It is probable that potassium purpurate is potassium nitrosonitrohydroxybenzonitrile, $NO{\cdot}C_6H_2(NO_2)(OK){\cdot}CN$. *Potassium* o-*tolylpurpurate*, [*potassium* 1-*methyl*-4-*cyano*-3-*nitroso*-5-*nitrophenoxide* (?)], obtained by the action of a warm concentrated solution of potassium cyanide on an alcoholic solution of dinitro-*o*-cresol, and purified by crystallisation from dilute potassium cyanide, is a dark-red, crystalline powder readily soluble in water but insoluble in alcohol or ether. Nitric acid decomposes it, yielding nitrogen oxides and *dinitrohydroxytoluonitrile*,

$$[CN : OH : Me : (NO_2)_2 = 1 : 3 : 4 : 2 : 6],$$

which crystallises in yellow, glistening needles melting at 148—149°; it yields a *potassium* derivative crystallising in dark yellow needles which explode when heated.

The nitrile combines with aniline, yielding an *additive* product, $C_8H_5O_5N_3,C_6H_7N$, which crystallises from water in yellow, glistening plates melting at 156—158°. On hydrolysis with potassium hydroxide, the nitrile yields the corresponding amide, *dinitrohydroxytoluamide*, $OH{\cdot}C_6HMe(NO_2)_2{\cdot}CONH_2$, in the form of glistening crystals melting at 231°, and also yielding a compound with aniline.

Potassium p-*tolylpurpurate* crystallises from 1 per cent. potassium cyanide in microscopic, brown needles, and on treatment with sodium nitrite and acetic acid yields an *acid*, the *silver* salt of which has the formula $C_9H_5O_9N_5Ag_2$. J. J. S.

Ketone and Acid Decomposition in the Ethyl Acetoacetate Series. By EMIL KNOEVENAGEL [and, in part, A. FRIES] (*Ber.*, 1902, **35**, 392—395).—Ethyl benzylidenebisacetoacetate, *p*-methylbenzylidenebisacetoacetate, and furfurylidenebisacetoacetate are decomposed by alkalis in the normal manner; with dilute alkalis, *cyclo*hexenones are mainly formed, whilst with concentrated alkalis *β*- substituted glutaric acids are the chief products. Thus when ethyl benzylidenebisacetoacetate was boiled with a 10 per cent. potassium hydroxide solution, 73 per cent. of 3-phenyl-1-methyl-5-*cyclo*hexenone and 17 per cent. of *β*-phenylglutaric acid were formed; with 60 per cent. potassium hydroxide, 4 per cent. of the ketone and 87 per cent. of the acid were obtained.

Ethyl *m*- and *p*-nitrobenzylidenebisacetoacetate, even with a 2 per cent. solution of potassium hydroxide, only yield the corresponding *β*-glutaric acids. On the other hand, ethyl citrylidene- and ethyl citronellidene-bisacetoacetates are not attacked by dilute alkalis, and with concentrated (80 per cent.) aqueous or alcoholic solutions only give ketones.

β-Furfurylglutaric acid, $CO_2H{\cdot}CH_2{\cdot}CH(C_4OH_4){\cdot}CH_2{\cdot}CO_2H$, forms crystals melting at 134—135°. K. J. P. O.

Condensing Action of Organic Bases. By EMIL KNOEVENAGEL and E. SPEYER (*Ber.*, 1902, **35**, 395—399).—Ethyl acetoacetate and dibenzylideneacetone condense in alcoholic solution at the ordinary temperature in the presence of a small quantity of diethylamine, forming *ethyl dibenzylideneacetone-acetoacetate*,

$$CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH(COMe){\cdot}CO_2Et,$$

which crystallises in white needles melting at 132°. When treated with dry hydrogen chloride in chloroform solution or boiled with sodium hydroxide, *ethyl 3-cinnamenyl-5-phenyl-Δ^2-ketotetrahydrobenzene-6-carboxylate*, $CHPh{:}CH{\cdot}C{<}\begin{matrix} CH_2{\cdot}CHPh \\ CH\text{———}CO \end{matrix}{>}CH{\cdot}CO_2Et$, is produced; it crystallises in yellow plates melting at 134°.

Ethyl benzylideneacetophenone-acetoacetate,

$$COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CH(COMe){\cdot}CO_2Et,$$

prepared from benzylideneacetophenone and ethyl acetoacetate, crystallises in small, white needles melting at 120—121° and is converted by hydrogen chloride or sodium ethoxide into ethyl 3 : 5-diphenyl-Δ^2-ketotetrahydrobenzene-6-carboxylate (m. p. 111—112°, Abstr., 1895, i, 48). Benzylideneacetone and ethyl acetoacetate yield ethyl benzylidenebisacetoacetate (m. p. 152°, *loc. cit.*). K. J. P. O.

Methyl Derivatives of Indigotin. By MITSURU KUHARA and MASUMI CHIKASHIGÉ (*Amer. Chem. J.*, 1902, **27**, 1—15. Compare Abstr., 1900, i, 560).—*Chloroacetylmethylanilide*, $CH_2Cl{\cdot}CO{\cdot}NMePh$, obtained by mixing chloroacetyl chloride with methylaniline, both in ethereal solution, crystallises from hot water in prisms and melts at 61°. When fused with potassium hydroxide, it is completely decomposed without giving any substance related to indigotin.

Chloroacetyl-m-*toluidide*, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$, melting at 141°, was prepared from chloroacetyl chloride and *m*-toluidine. From the *o*- and *p*-compounds, diaryldiketopiperazines were prepared, and these, when fused with potassium hydroxide, gave dimethylindigotins.

5 : 5′-*Dimethylindigotin* can be obtained from chloroacetyl-*o*-toluidide or from di-*o*-tolyldiketopiperazine as a powder, which, when sublimed, crystallises in prisms closely resembling ordinary indigo in appearance. One gram of it is soluble in about 2000 c.c. of alcohol, or in 500 c.c. of chloroform; it is also soluble in ether, aniline, benzene, acetic acid, sulphuric acid, &c.

7 : 7′-*Dimethylindigotin* was similarly obtained from the corresponding para-compounds and 6 : 6′-*dimethylindigotin* from chloroacetyl-*m*-toluidide.

Chloroacetyl-as-m-*xylidide*, $C_6H_3Me_2{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, which melts at 143°, when treated with alcoholic potash, gives *di*-as-m-*xylyldiketopiperazine*, which melts at 170°; both of these, when fused with potassium hydroxide, give 5 : 7 : 5′ : 7′-*tetramethylindigotin*.

4 : 5 : 7 : 4′ : 5′ : 7′-*Hexamethylindigotin* was similarly obtained from *chloroacetyl-ψ-cumidide*, melting at 158·5°, which is prepared from chloroacetyl chloride and *ψ*-cumidine. The same indigotin derivative is obtained from di-*ψ*-cumidyldiketopiperazine (m. p. 221·5°).

The following positions of maximum darkness in the absorption bands of these various indigotins have been determined:

	λ_1	λ_2	$\frac{\lambda_1+\lambda_2}{2}$
Indigotin	622·7	587·6	605·1
5 : 5′-Dimethylindigotin	643·6	615·7	629·7
6 : 6′-Dimethylindigotin	619·2	598·1	608·6
7 : 7′-Dimethylindigotin	642·7	622·7	633·2
5 : 7 : 5′ : 7′-Tetramethylindigotin	662·7	631·7	647·2

The colours of solutions of these indigotins in various solvents are also given. J. McC.

Derivatives of 3-Nitrophthalic Acid. By ROBERT KAHN (*Ber.* 1902, **35**, 471—472).—Contrary to the statement of Seidel (this vol., i, 159) both the possible nitroanthranilic acids (Hubner, Abstr., 1878, 148; 1880, 549) are formed by the action of hypobromite on 3-nitrophthalimide. T. M. L.

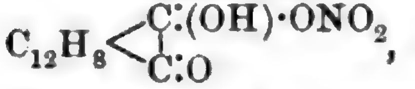
Usnic Acid: Rotatory Power of other Lichen Derivatives. By HEINRICH SALKOWSKI (*Annalen*, 1901, **319**, 391—399. Compare Abstr.,1901, i, 152).—Hesse's contention that *Usnea longissima* contains *d*-usnic acid is confirmed. The *l*-acid from *Cladonia destricta*, *C. uncialis*, and *C. incrassata* has a mean $[\alpha]_D$ −489·2°, whilst that from *Placodium crassum* has $[\alpha]_D$ −477·3°. Leprarin, stictaurin, and placodiolin have rotatory powers 13·4°, −9·9°, and −238·4°. Glomellic acid and stereocaulic acid are inactive.

Usnidic acid, obtained by Hesse by the fusion of usnic acid with potash (Abstr., 1901, i, 595), is identical with the author's usnetic acid. The latter designation has already been applied by Hesse to another product (Abstr., 1901, i, 645). The phenolic decomposition product, usnetol, obtained from the author's usnetic acid, is probably identical with the usnetol prepared by Paternò from pyrousnic acid. In preparing Paternò's pyrousnic acid, the readily oxidisable alkaline solution must be heated in an atmosphere of hydrogen, and not in oxygen as indicated in "Beilstein," II., 2058, 3rd edition. G. T. M.

Compounds of Aromatic Aldehydes and the Esters of Aromatic Acids with Orthophosphoric Acid and its Alkyl Esters. By P. N. RAIKOW and P. SCHTARBANOW (*Chem. Zeit.*, 1901, **25**, 1134—1138. Compare Abstr., 1900, i, 602, and 1901, i, 319).—In continuation of work previously published, the authors have prepared crystalline compounds of phosphoric acid with *p*-tolualdehyde and with vanillin, and also of phosphoric acid with methyl *p*-phthalate. The influence of the position and chemical nature of substituting groups on this capacity of forming compounds with phosphoric acid is discussed. K. J. P. O.

***cis*- and *trans*-Dibenzoylethylenes.** By CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1902, **35**, 168—176. See Abstr., 1901, i, 154).—*trans*-Dibenzoylethylene is quantitatively converted into the *cis*-form when its solution in some organic solvent is exposed to daylight, the time required varying with different solvents up to 96 hours of daylight. When treated with hydrogen chloride, both isomerides yield *chlorodiphenacyl*, $COPh{\cdot}CHCl{\cdot}CH_2{\cdot}COPh$, which crystallises from ethyl acetate in six-sided, monoclinic tablets, melts and decomposes at 141°, and, when treated with sodium acetate, gives the *trans*-isomeride, thus affording a means of converting the *cis*- into the *trans*-form. The corresponding *bromo*-derivative forms similar crystals and melts and decomposes at 139°. Hydrogen iodide converts the *trans*-form into diphenacyl. R. H. P.

Phenanthraquinone Nitrate. By Friedrich Kehrmann and M. Mattisson (*Ber.*, 1902, **35**, 343—344).—*Phenanthraquinone nitrate*,

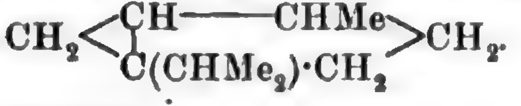


$C_{12}H_8<\begin{matrix}C{:}(OH){\cdot}ONO_2\\ |\\ C{:}O\end{matrix}$, obtained in lustrous, orange-red prisms by dissolving the quinone in nitric acid of sp. gr. 1·4, is readily decomposed into its generators by water. Phenanthraquinone combines with sulphuric acid in a similar manner; its solution in the concentrated acid has a yellowish-green colour, and probably contains a disulphate; on diluting slightly, the colour changes to yellowish-red, and a sulphate corresponding with the nitrate separates in red needles. Chrysoquinone behaves in a similar manner towards sulphuric acid. G. T. M.

Sesquiterpene of Eucalyptus Oils. By Henry G. Smith (*Chem. News*, 1902, **85**, 3).—Several eucalyptus oils contain in considerable quantity a sesquiterpene, *aromadendrene*, which boils at 260—265°, has a sp. gr. 0·9249 at 19°, and when mixed with acetic acid and treated with bromine gives a crimson colour, changing through violet to deep indigo blue. It is this substance which gives the pink coloration when eucalyptus oils are tested for eucalyptol with phosphoric acid. D. A. L.

Oil of Jasmine Blossoms. By Ernst Erdmann (*Ber.*, 1902, **35**, 27—30).—This communication is mainly polemical (compare Hesse, Abstr., 1900, i, 48, 454; 1901, i, 220, 732; and Erdmann, Abstr., 1901, i, 601). G. T. M.

A New Constituent of German Oil of Sage. By Heinrich Seyler (*Ber.*, 1902, **35**, 550—552. Compare Wallach, *Annalen*, **227**, 289; **252**, 104).—*Salvene*, $C_{10}H_{18}$, a liquid hydrocarbon, boiling at 142—145°, has been obtained from German oil of sage. It has a sp. gr. 0·80 at 20°, n_D 1·4438, and a rotation of +1°40′. When treated with 25 per cent. sulphuric acid, the boiling point of the hydrocarbon is raised some 18—20°, and, when oxidised with permanganate, a ketonic acid is obtained the semicarbazone of which melts at 204°, whereas β-tanacetoketonic acid semicarbazone melts at 202°. The hydrocarbon *salvene* probably contains a bridged ring and has the formula



$CH_2<\begin{matrix}CH\text{———}CHMe\\ |\\ C(CHMe_2){\cdot}CH_2\end{matrix}>CH_2$. J. J. S.

Oxygen Bases. By GEORG BREDIG (*Ber.*, 1902, **35**, 271. Compare Walker, this vol., i, 170).—The author has already pointed out (*Zeit. Elektrochem.*, 1896, **3**, 116) that ethylene oxide has only feebly basic properties. J. J. S.

Dehydromucic Acid [Furfurandicarboxylic Acid]. By BERNHARD TOLLENS (*Ber.*, 1902, **35**, 98).—A question of priority in the methods of formation of furfurandicarboxylic acid from mucic acid by means of acids (compare Yoder and Tollens, this vol., i, 49, and Hill, Abstr., 1901, i, 555). K. J. P. O.

Action of Methylamine and Ethylamine on Furfuraldehyde and Cuminaldehyde. By G. SCHWABBAUER (*Ber.*, 1902, **35**, 410—415. Compare Zaunschirm, Abstr., 1888, i, 1077).—*Furfurylidenemethylamine*, $C_4OH_3\cdot CH\colon NMe$, is formed when furfuraldehyde is mixed with aqueous methylamine, and is a colourless oil boiling at 63° under 14 mm. pressure. On reduction with sodium and alcohol, *methylfurfurylamine*, $C_4OH_3\cdot CH_2\cdot NMe$, is obtained as an oil boiling at 65—67° under 21 mm. pressure; the *hydrochloride* of the base crystallises in white leaflets with a silky lustre melting at 139°; the *hydrobromide* crystallises in small, white needles or leaflets melting at 131°; the *picrate* in yellow needles melting at 144°. *Furfurylidene-ethylamine*, $C_4OH_3\cdot CH\colon NEt$, is a colourless oil of disagreeable odour, boiling at 60—63° under 14 mm. pressure; *furfurylethylamine*, $C_4OH_3\cdot CH_2\cdot NHEt$, is an oil boiling at 49—50° under 21 mm. pressure; the *hydrochloride* of the latter crystallises in white plates melting at 120°; the *hydrobromide* in small, lustrous needles melting at 113°; the *picrate* in yellow needles melting at 111°.

From cuminaldehyde and methylamine is obtained *cumylidenemethylamine*, $C_6H_4Pr^\beta\cdot CH\colon NMe$, which is an oil boiling at 122° under 14 mm. pressure. On reduction, *cumylmethylamine*,

$$C_6H_4Pr^\beta\cdot CH_2\cdot NHMe,$$

is produced as a colourless oil of pleasant odour boiling at 121° under 23 mm. pressure; its *hydrochloride* crystallises in white needles melting at 165°; the *hydrobromide* in large, white plates melting at 178°; the *platinichloride* in small, yellow needles melting at 193°; the *aurichloride* in small, yellow needles melting at 141°, and the *picrate* in yellow needles melting at 137°.

Cumylidene-ethylamine, $C_6H_4Pr^\beta\cdot CH\colon NEt$, is a golden-yellow oil, boiling at 149° under 19 mm. pressure; the product of reduction, *cumylethylamine*, $C_6H_4Pr^\beta\cdot CH_2\cdot NHEt$, is an oily base of pleasant odour boiling at 132° under 19 mm. pressure; its *hydrochloride* crystallises in silver-white plates melting at 180°; the *hydrobromide* in white plates melting at 196°; the *aurichloride* in small, yellowish-green needles melting at 131°; the *platinichloride* in reddish-yellow plates melting at 179°, and the *picrate* in yellow plates melting at 122°. K. J. P. O.

Basic Properties of Sulphur. By ALBERT EDINGER and JOHN B. EKELEY (*Ber.*, 1902, **35**, 96—98. Compare Abstr., 1901, i, 166, 753).—The compounds obtained from aromatic bases and sulphur chloride are now believed by the authors to contain two quadrivalent basic sulphur atoms, and in consequence to have two additional hydrogen atoms respectively attached to the two sulphur atoms in the sulphur ring, $\begin{array}{c}C\cdot SH\cdot C\\ |\quad\ |\quad\ |\\ C\cdot SH\cdot C\end{array}$. Analyses are given of the *tetranitrate* of thioquinanthrene, $C_{18}H_{12}N_2S_2,4HNO_3,2H_2O$, the *tetranitrate* of the base from sulphur chloride and *o*-toluquinoline, $C_{18}H_{12}N_2S_2,4HNO_3,2H_2O$, and the *tetranitrate* of *p*-toluthioquinanthrene, $C_{20}H_{16}N_2S_2,4HNO_3$. With acetyl chloride, the hydrochlorides of acetyl derivatives are obtained, in which the acetyl group is attached to sulphur. The *hydrochlorides* of acetylthioquinanthrene, $C_{22}H_{16}O_2N_2S_2,2HCl$, of the acetyl derivative of the base from *o*-toluquinoline, $C_{22}H_{16}O_2N_2S_2,2HCl$, and of acetyl-*p*-toluthioquinanthrene, $C_{24}H_{20}O_2N_2S_2,2HCl$, have been analysed.

The *disulphate* of thioquinanthrene has the formula

$$C_{18}H_{12}N_2S_2,2H_2SO_4;$$

that of *p*-toluthioquinanthrene, $C_{20}H_{16}N_2S_2,2H_2SO_4,2H_2O$, is red, but when anhydrous, it forms a yellow solid. K. J. P. O.

Arginine and Ornithine. By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1901, **34**, 128—147. Compare Abstr., 1900, i, 110).—Ornithine chloride is optically active, $[\alpha]_D$ +15·64—16·8°. The *platinichloride*, $C_5H_{12}O_2N_2,H_2PtCl_6$, forms a microcrystalline precipitate; the *picrate*, $C_5H_{12}O_2N_2,C_6H_3O_7N_3$, crystallises in stellate aggregates of prisms or in large, flat plates, and the *phosphotungstate* forms a precipitate soluble in boiling water. Ornithine, like lysine, is not precipitated on the addition of silver nitrate and baryta water. From E. Fischer's work (Abstr., 1901, i, 191) and also from that of Kutscher, it is probable that arginine is guanidine-α-aminovaleric acid.

Arginine is not decomposed when boiled for several hours with concentrated hydrochloric acid; at 180—200° decomposition takes place and ammonium chloride is formed.

In the preparation of ornithine from arginine, the yield is not increased when other bases are substituted for baryta water. Sodium hypobromite readily decomposes arginine, and about one-third of the nitrogen is liberated. J. J. S.

Chelidoxanthin is Impure Berberine. By JULIUS O. SCHLOTTERBECK (*Pharm. Review*, 1902, **20**, 4—5. Compare this vol., ii, 100).—By a study of its colour reactions, solubility in various solvents, &c., it is shown that Probst's chelidoxanthin is nothing more than impure berberine. H. R. LE S.

Creatine and Creatinine. By ADOLF JOLLES (*Ber.*, 1902, **35**, 160—161).—Details of analyses which show that creatinine, like glycine (Abstr., 1901, i, 30), is comparatively stable towards permanganate in acid solution. This is explained by the assumption that both have a closed ring constitution of the nature of lactones.

R. H. P.

Identification and Properties of α- and β-Eucaine. By CHARLES L. PARSONS (*J. Amer. Chem. Soc.*, 1901, **23**, 885—893).—α-Eucaine melts at 103°, β-eucaine at 91°, and their hydrochlorides melt and decompose at about 200° and 268° respectively. Both these bases, like cocaine, are precipitated by ammonia, but α-eucaine is distinguished from the others by being almost insoluble in excess of the reagent. Potassium iodide gives a white, glistening precipitate with solutions of α-eucaine hydrochloride, but does not yield a precipitate with β-eucaine or cocaine. When potassium dichromate is added to a solution of α-eucaine, an almost insoluble, lemon-yellow precipitate is produced, which is increased on addition of hydrochloric acid; β-eucaine and cocaine are not precipitated by potassium dichromate until after the addition of hydrochloric acid, when a yellow precipitate appears which readily dissolves in excess of hydrochloric acid or on dilution with water.

If cocaine hydrochloride is triturated with dry mercurous chloride and then moistened with alcohol, it rapidly becomes greyish-black; α-eucaine slowly turns dark grey under these conditions, whilst β-eucaine is not affected. On addition of platinic chloride to a 1 per cent. solution of cocaine hydrochloride, a yellow, crystalline precipitate is produced, which is insoluble in hydrochloric acid, whilst solutions of α- and β-eucaine hydrochloride of the same strength do not yield a precipitate. When a small quantity of a solution of the hydrochloride is treated with a drop of potassium permanganate solution, in the case of the eucaines the solution rapidly turns brown, whilst with cocaine the colour is not completely changed in half-an-hour.

β-Eucaine hydrochloride is distinguished from cocaine hydrochloride by its comparative insolubility in water or alcohol.

The microscopic characters of the hydrochlorides of the three alkaloids under polarised light are described. E. G.

Pilocarpine. By ADOLF PINNER and R. SCHWARTZ (*Ber.*, 1902, **35**, 192—210. Compare Pinner and Kohlhammer, Abstr., 1900, i, 456, 685; 1901, i, 340; Jowett, Trans., 1901, **79**, 1331).—The experiments made by Pinner and Kohlhammer have been repeated and the results confirmed with the exception that piluvic acid, or *homopilomalic acid* as the authors prefer to call it, is probably $C_8H_{14}O_5$ and not $C_8H_{12}O_5$.

The amide of piluvic acid melts at 206°; Jowett gives 208°.

When pilocarpine or *iso*pilocarpine is oxidised at the ordinary temperature with potassium permanganate (3 mols.), the chief product is the acid $C_8H_{14}O_5$; when chromic acid is employed, an acid, $C_{11}H_{16}O_5N_2$, is obtained which, on oxidation with permanganate at the ordinary temperature, yields an acid, $C_7H_{12}O_5$, previously described as *iso*hydrochelidonic acid, but now called *pilomalic acid.*

The acid, $C_7H_{12}O_5$, when heated at its melting point, loses a mol. of water yielding a non-crystallisable dibasic *acid*, $C_7H_{10}O_4$, isomeric with Jowett's pilopic acid; this gives a *barium* salt, $C_7H_{10}O_5Ba$ or $C_7H_8O_4Ba$. Pilomalic acid is lævorotatory and has $[\alpha]_D$ −11·7°.

A solution of *iso*pilocarpic acid may be obtained by passing carbon dioxide into an absolute alcoholic solution of its salt and filtering off the alkali carbonate. When the solution is warmed, *iso*pilocarpine is formed, but when concentrated under reduced pressure, a substance, $C_{11}H_{18}O_3N_2,H_2O$, is obtained.

iso*Pilocarpic acid platinichloride* forms nodular crystals melting at 180°. Pilocarpic acid cannot be isolated from its salts in a similar manner and also differs from *iso*-acid in that its hydrochloride yields no precipitate with mercuric chloride. Both acids in the free state combine with mercuric chloride, yielding compounds of the formula $C_{11}H_{16}O_2N_2,HgCl_2$; the one from pilocarpic acid softens at 127° and melts at 145°, that from *iso*-acid melts at 164°. No definite additive compound of pilocarpine and bromine has been prepared. Even when only 2 atoms of bromine in chloroform solution are employed for 1 molecule of the base, the resulting product is dibromopilocarpine, whilst with a larger amount of bromine, the perbromide,

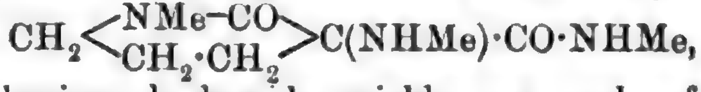
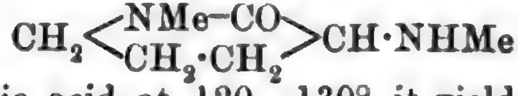
$$C_{11}H_{14}O_2N_2Br_2,HBr_3,$$

is formed. Dibromopilocarpine, $C_{11}H_{14}O_2N_2Br_2$, melts at 94° and not at 79° as previously stated. Bromocarpic acid has been obtained in a crystalline state (compare Jowett, *loc. cit.*); it melts at 209° and not at 194° and has $[\alpha]_D$ $-90{\cdot}5°$.

The indifferent substance previously obtained by the oxidation of pilocarpine with permanganate is probably methylcarbamide.

Pilocarpine crystallises in long needles melting at 34°. J. J. S.

Yohimbine. By Carl Arnold and M. Behrens (*Chem. Zeit.*, 1901, **25**, 1083).—Yohimbine hydrochloride, $C_{22}H_{28}O_3N_2,HCl$, obtained from the bark of the Yohimbehe, a tree of the Cameroons, closely resembles cocaine hydrochloride in physiological action. The authors have made a careful comparison of the chemical and physical characters of the two salts. K. J. P. O.

Formation of the Pyrrolidine Ring. By Richard Willstätter and Friedrich Ettlinger (*Ber.*, 1902, **35**, 620—622. Compare Abstr., 1900, i, 405).—Ethyl dibromopropylmalonate and methylamine yield the methylamide  $CH_2<\begin{matrix}NMe-CO\\CH_2\cdot CH_2\end{matrix}>C(NHMe)\cdot CO\cdot NHMe$, which, on hydrolysis with barium hydroxide, yields one mol. of methylamine and the methylamide  $CH_2<\begin{matrix}NMe-CO\\CH_2\cdot CH_2\end{matrix}>CH\cdot NHMe$ whereas on hydrolysis with hydrochloric acid at 120—130° it yields 1-methylpyrrolidine-2-carboxylic acid, in the form of its hydrochloride. J. J. S.

Cyclic Quaternary Ammonium Salts. By Edgar Wedekind (*Ber.*, 1902, **35**, 178—185. Compare Menschutkin, Abstr., 1895, ii, 385; Evans, Trans., 1897, **71**, 552).—1-*Benzylpiperidinium iodide ethyl acetate*, obtained by the combination of benzylpiperidine and ethyl iodoacetate or of ethylpiperidinoacetate and benzyl iodide, crystallises from a mixture of chloroform and benzene or chloroform and acetone in monoclinic, prismatic needles melting at 193—194° [$a:b:c = 1{\cdot}6160:1:0{\cdot}8215$; $\beta = 84°11'$]. It dissolves readily in warm alcohol or water. The corresponding bromide, formed by the combination of benzylpiperidine and ethyl bromoacetate or of ethyl piperidinoacetate and benzyl bromide (Abstr., 1901, i, 639), melts at 192°.

Methyl piperidine-1-*acetate*, $C_8H_{15}O_2N$, obtained by the action of methyl chloroacetate on piperidine, is a colourless oil distilling at 205—207°, which combines with benzyl bromide to form a *quaternary* salt melting at 193—194°, identical with the product obtained from benzylpiperidine and methyl bromoacetate.

Benzylallylpiperidinium bromide, $C_3H_5{\cdot}C_5NH_{10}Br{\cdot}C_7H_7$, obtained from 1-benzylpiperidine and allyl bromide, forms colourless prisms decomposing at 161°.

1-*Allyltetrahydroquinoline* may be obtained by the action of allyl bromide or iodide on tetrahydroquinoline, or by the reduction of quinoline allyl iodide with tin and hydrochloric acid; it is a pale yellow liquid boiling at 264—266° under 755 mm. pressure; the *hydrobromide* crystallises from alcohol and melts at 164—165°.

Methylallyltetrahydroquinolinium iodide, obtained by the combination of kairoline with allyl iodide or of 1-allyltetrahydroquinoline with methyl iodide, crystallises in yellowish, monoclinic prisms [$a:b:c = 0{\cdot}6677:1:0{\cdot}4957$; $\beta = 70°28{\cdot}5'$]. It decomposes at 143° and is readily soluble in warm water, alcohol, or chloroform.

1-*Benzyltetrahydroquinoline* distils at 218—222° under 38 mm. pressure, crystallises from alcohol in colourless needles melting at 36—37°, and combines only slowly with ethyl iodide. J. J. S.

Condensation of 6-Phenyl-2-methylpyridine with Aldehydes.

By E. THORAUSCH (*Ber.*, 1902, **35**, 415—419. Compare Dehnel, Abstr., 1901, i, 165).—6-*Phenyl-2-o-nitrostilbazole*, $C_5NH_3Ph{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, prepared by condensing 6-phenyl-2-methylpyridine with *o*-nitrobenzaldehyde, crystallises from dilute alcohol in yellow needles and melts at 62°; the *hydrochloride* forms lemon-yellow, hair-like crystals and melts at 186—187°; the *hydrobromide* forms yellow needles and melts at 238°; the *aurichloride*, $(C_{19}H_{14}O_2N_2,HCl)_2AuCl_3,2H_2O$, forms yellow needles and melts at 126°; the *platinichloride* forms short, orange-red needles and melts at 200°; the *mercurichloride* crystallises from dilute alcohol in white needles and melts at 219°.

The *dibromide*, $C_6NH_5Ph{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_4{\cdot}NO_2$, crystallises from dilute alcohol in white needles and melts at 145°.

6-*Phenyl-2-m-nitrostilbazole*, prepared in a similar manner to the *o*-compound, forms yellow needles and melts at 139°; the *hydrochloride* forms long, slender, yellow needles and melts at 216°; the *hydrobromide* crystallises from dilute alcohol in small, pale yellow needles and melts at 263°; the *aurichloride*, $C_{19}H_{14}O_2N_2,HCl,AuCl_3$, forms yellow needles, dissolves readily in hot alcohol, and melts at 178—179°; the *platinichloride* forms small, orange-coloured needles, does not dissolve readily in alcohol, and melts at 262°.

The *dibromide*, $C_{19}H_{14}O_2N_2Br_2$, crystallises from hot alcohol in white needles, and melts at 189°.

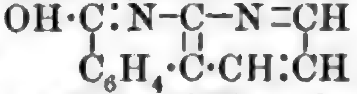
6-*Phenyl-2-piperonylalkidine*, $C_5NH_3Ph{\cdot}CH{:}CH{\cdot}C_6H_3{<}^{O}_{O}{>}CH_2$, prepared by condensing phenylmethylpyridine with piperonaldehyde, crystallises from dilute alcohol in white needles and melts at 155°; the *hydrochloride* crystallises from dilute alcohol in yellow needles and melts at 239°; the *aurichloride* forms golden-yellow needles, but decomposes on recrystallising; the *platinichloride* forms yellow needles and melts at 242°.

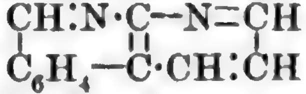
By the action of bromine on the base, a *substance* is obtained which crystallises in white needles, melts at 117°, and appears to be formed from the dibromide by loss of a mol. of hydrogen bromide.

6-*Phenyl-o-nitro-2-β-hydroxyphenethylpyridine*,

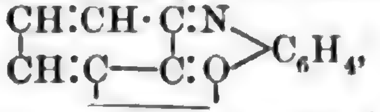
$$C_5NH_3Ph\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot NO_2,H_2O,$$

the hydrochloride of which is formed from phenylmethylpyridine and *o*-nitrobenzaldehyde under slightly altered conditions, crystallises from dilute alcohol in white needles, sinters at 65°, and melts at 95°; the *hydrochloride* forms short, yellow needles, dissolves fairly readily in water, and melts at 182°; the *aurichloride* crystallises from dilute alcohol in yellow needles and melts at 175°; the *platinichloride* forms orange-red needles, crystallises from dilute alcohol with $2H_2O$, and melts at 156°. T. M. L.

***iso*Quino-β-pyridine.** By WILHELM MARCKWALD and H. DETTMER (*Ber.*, 1902, **35**, 296—302).—3-Phenylpyridine-2 : 2′-dicarboxylic acid (Skraup and Cobenzl, Abstr., 1883, 1010) yields its *anhydride* when dissolved in acetic anhydride at 120°; the product separates from hot benzene in white crystals melting at 183°, and is converted by aqueous ammonia into 3-*phenylpyridine-2 : 2′-dicarboxylamic acid*, $CO_2H\cdot C_6H_4\cdot C_5NH_3\cdot CO\cdot NH_2$, which forms white crystals, melts at 200°, and yields crystalline salts with both acids and alkalis; the *picrate*, melting at 174°, the *dichromate*, and the *silver* salt were analysed. The amide is converted by warm aqueous sodium hypobromite into 6-*hydroxyisoquino-β-pyridine*,  $\begin{array}{l} OH\cdot C\colon N-C-N=CH \\ C_6H_4\cdot C\cdot CH\colon CH \end{array}$, which crystallises in white, felted needles, melts at 274—276° and sublimes at a higher temperature; the *picrate*, melting and decomposing at 260°, and the *platinichloride* were analysed. Its structure and that of the original amide follow from its yielding phthalic acid, not quinolinic acid, on oxidation.

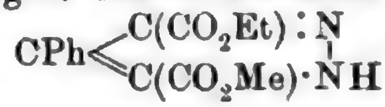
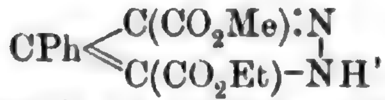
6-*Chloroisoquino-β-pyridine*, obtained by heating the hydroxy-compound with phosphorus pentachloride and oxychloride for 4—5 hours at 180°, crystallises from toluene in yellowish-brown needles, melts at 182—183°, and yields a *picrate* decomposing at 240°; when heated for 5 hours with concentrated hydriodic acid and phosphorus, it is reduced to *isoquino-β-pyridine*,  $\begin{array}{l} CH\colon N\cdot C-N=CH \\ C_6H_4-C\cdot CH\colon CH \end{array}$, which crystallises from alcohol, melts at 113—114°, boils unchanged above 360°, and is a mono-acid base; the *hydrochloride*, $C_{12}H_8N_2,HCl,2H_2O$, melts at first at 99°, or when anhydrous at 207°, the *picrate* melting at 213°, and the *dichromate* at 170°. W. A. D.

The Simplest Azoxone. By FRIEDRICH KEHRMANN and A. SAAGER (*Ber.*, 1902, **35**, 341—342).—*Phenazoxone*,



$$\begin{array}{l} CH\colon CH\cdot C\colon N \\ CH\colon C-C\colon O \end{array}\!\!>C_6H_4,$$

produced by oxidising phenoxazine with ferric chloride in glacial acetic acid solution, crystallises from water in lustrous, yellowish-brown leaflets melting at 216—217°; it is only feebly basic, its salts being completely dissociated by water. The substance is insoluble in solutions of the alkali hydroxides, but dissolves in benzene or alcohol. G. T. M.

Pyrazole Derivatives. By Eduard Buchner and Carl von der Heide (*Ber.*, 1902, **35**, 31—34).—Methyl ethyl 4-phenylpyrazoline-3 : 5-dicarboxylate, produced by adding methyl diazoacetate to ethyl cinnamate, and its isomeride, obtained from ethyl diazoacetate and methyl cinnamate (Buchner and Dessauer, Abstr., 1893, i, 282), when treated with bromine in chloroform solution, give rise to the same *methyl ethyl 4-phenylpyrazole-3 : 5-dicarboxylate*,  $\mathrm{CPh}<\begin{array}{l}\mathrm{C(CO_2Et):N}\\ \mathrm{C(CO_2Me)\cdot NH}\end{array}$ or  $\mathrm{CPh}<\begin{array}{l}\mathrm{C(CO_2Me):N}\\ \mathrm{C(CO_2Et)-NH}\end{array}$, this substance separating in rhombohedral crystals or needles melting at 105° and yielding 4-phenylpyrazole-3 : 5-dicarboxylic acid on hydrolysis with hydrochloric acid. The acid, when heated, loses carbon dioxide, giving rise to 4-phenylpyrazole. G. T. M.

Pyrazole-4-carboxylic Acid from 4-Phenylpyrazole. By Wilhelm Behaghel and Eduard Buchner (*Ber.*, 1902, **35**, 34—35).—Pyrazole-4-carboxylic acid (Buchner and Fritsch, Abstr., 1893, i, 432) is produced in small amount from 4-phenylpyrazole by successively nitrating the base to a dinitro-derivative, reducing the product to the amine, and oxidising this with potassium permanganate solution; the acid is isolated from the products of oxidation in the form of its copper salt, this being subsequently decomposed by hydrogen sulphide; it decomposes at 275° and yields pyrazole by loss of carbon dioxide. G. T. M.

Phenylacetylene and Alkyl Diazoacetates. By Eduard Buchner and Louis Lehmann (*Ber.*, 1902, **35**, 35—37).—*Ethyl 5 : 3-phenylpyrazolecarboxylate*,* $C_3N_2H_2Ph\cdot CO_2Et$, obtained by heating together on the water-bath phenylacetylene and ethyl diazoacetate, separates from ether in colourless crystals and melts at 140°. The corresponding *methyl* ester produced from phenylacetylene and methyl diazoacetate melts at 181—182°. These esters, on hydrolysis, yield 5 : 3-phenylpyrazolecarboxylic acid, which melts at 233—234° (compare Knorr and Sjollema, Abstr., 1894, i, 546) and readily gives rise to 5-(or 3-)phenylpyrazole on heating at 140—150°. G. T. M.

5 : 3-Pyrazolecarboxylic Acid from 5-(or 3-)Phenylpyrazole. By Eduard Buchner and Christophor Hachumian (*Ber.*, 1902, **35**, 37—42. Compare preceding abstract).—5-(or 3-)Phenylpyrazole is the only product of the action of hydrazine hydrate on benzoylaldehyde (Knorr, 1895, i, 395; von Rothenburg, 1895, i, 303), and is most readily prepared by this method.

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* It is uncertain which group is in the 3-, which in the 5-position.

5-(or 3-)*Nitrophenylpyrazole nitrate*, $NO_2 \cdot C_6H_4 \cdot C_3N_2H_3, HNO_3$, separates in yellow needles when 5-(or 3-)phenylpyrazole is added to cold fuming nitric acid; it decomposes at 182—184° and is decomposed on treatment with water or alkaline solutions into nitro-5-(or 3-)phenylpyrazole (Knorr, Abstr., 1894, i, 546).

5-(or 3-)*Dinitrophenylpyrazole*, obtained on nitrating 5-(or 3-)phenylpyrazole on the water-bath, forms colourless needles decomposing at 212°; with solutions of the alkali hydroxides, it yields metallic derivatives, the *sodium* compound, $C_9H_5O_4N_4Na$, crystallising in lemon-yellow needles.

5-(or 3-)*Aminophenylpyrazole*, $NH_2 \cdot C_6H_4 \cdot C_3H_3N_2$, resulting from the reduction of the nitro-compound with tin and hydrochloric acid, forms colourless needles melting at 104° and boiling at 290—300° under 12 mm. pressure; the *hydrochloride* and *sulphate* form colourless needles, the latter decomposing at 242°. The *platinichloride* separates in golden-yellow needles containing $2H_2O$; it melts at 105—110°; the *oxalate*, $(C_9H_9N_3)_2H_2C_2O_4$, with H_2O, melts at 165°, and the *picrate*, with $1\frac{1}{2}H_2O$, becomes anhydrous at 110°. 5-(or 3-)*Acetylaminophenylpyrazole*, $C_9H_8N_3Ac$, and the corresponding *benzoyl* derivative and the *thiocarbamide*, $(C_9H_8N_3)_2{:}CS$, crystallise in colourless needles and melt respectively at 207°, 227°, and 200—202°; 5-(or 3-)*benzylideneaminophenylpyrazole*, $C_9H_7N_3{:}CHPh$, is a white powder which melts somewhat indefinitely at 65° and is decomposed by water into its generators.

5-(or 3-)*Trimethylaminophenylpyrazoledimethiodide*, $C_9H_6N_3Me_3, 2MeI$, obtained by heating the base with methyl iodide at 120°, crystallises from methyl alcohol in colourless needles and melts at 211°.

5-(or 3-)*Tribromoaminophenylpyrazole*, $C_9H_6N_3Br_3$, produced by treating the base with bromine in ethereal solution, separates from this solvent in colourless needles and melts at 207°.

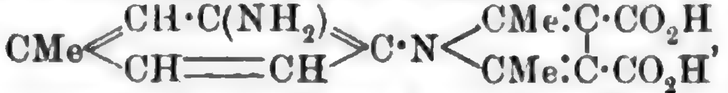
Pyrazole-5-(or 3-)carboxylic acid, prepared by oxidising 5-(or 3-) aminophenylpyrazole with a cold alkaline solution of permanganate, is separated in the form of its copper salt and isolated from this derivative by the action of hydrogen sulphide.

An oily phenylpyrazoline was stated to be formed by the action of hydrazine hydrate on cinnamaldehyde (Rothenburg, Abstr., 1894, i, 348; 1895, i, 302). On repeating this experiment, it was found that 5-(or 3-)phenylpyrazole was the only recognisable product.

G. T. M.

Relative Difference in Basicity of the Two Amino-groups of Substituted Diamines. By CARL BÜLOW and GEORG LIST (*Ber.*, 1902, **35**, 185—192. Compare Abstr., 1900, i, 690; Tiemann, *Ber.*, 1870, **3**, 221).—*o*-Tolylenediamine hydrochloride $[Me : (NH_2)_2 = 1:3:4]$ and ethyl diacetylsuccinate readily react in alcohol-acetic acid solution, yielding *ethyl o-tolylene-bis 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate*, $C_6H_3Me[C_4NMe_2(CO_2Et)_2]_2$, as a resinous product, which, on hydrolysis, yields the *tetracarboxylic acid* melting and decomposing at 272° and only very sparingly soluble in the usual organic solvents. The *acid silver* salt, $C_{23}H_{20}O_8N_2Ag_2$, has been prepared. The amount of alkali required to neutralise the acid, using phenolphthalein as indicator, corresponds with a di- and not with a tetra-basic acid.

Aminotolyl-2 : 5-dimethylpyrroledicarboxylic acid,



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{\cdot}C(NH_2)}\\ \mathrm{CH{=\!=\!=}CH}\end{matrix}{>}\mathrm{C{\cdot}N}{<}\begin{matrix}\mathrm{CMe{:}C{\cdot}CO_2H}\\ \mathrm{CMe{:}C{\cdot}CO_2H}\end{matrix},$$

is formed when molecular proportions of *o*-tolylenediamine hydrochloride and ethyl diacetylsuccinate are boiled for half-an-hour in an alcohol-acetic acid solution, and the resulting ester hydrolysed. It crystallises from alcohol in small needles, melts and decomposes at 205°, and is only sparingly soluble in the usual solvents. An *acid ammonium* and an *acid silver* salt have been prepared. The constitution of the acid has been established by the removal of the amino-group and conversion of the acid into Knorr's *p*-tolyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid (Abstr., 1885, 555).

It would thus appear that the amino-group in the *para*-position to the methyl group is the more strongly basic of the two amino-groups in *o*-tolylenediamine $[\mathrm{Me}:(\mathrm{NH_2})_2 = 1:3:4]$. J. J. S.

Derivatives of Toluene-*p*-sulphonic Chloride and *o*-Nitrotoluene-*p*-Sulphonic Chloride. By Frédéric Reverdin and Pierre Crépieux (*Ber.*, 1902, **35**, 314—315. Compare Abstr., 1901, i, 686).—*Bis-toluene*-p-*sulphon*-o-*phenylenediamide*, $C_6H_4(NH{\cdot}SO_2{\cdot}C_6H_4Me)_2$, obtained by boiling together toluene-*p*-sulphonic chloride and *o*-phenylenediamine in alcoholic solution, crystallises from this solvent in white needles and melts at 201—202°.

Bis-o-*nitrotoluene*-p-*sulphon*-o-*phenylenediamide*,

$$C_6H_4(NH{\cdot}SO_2{\cdot}C_6H_3Me{\cdot}NO_2)_2,$$

prepared from *o*-nitrotoluene-*p*-sulphonic chloride and *o*-phenylenediamine, crystallises from dilute acetic acid in white needles melting at 162—163°; like the preceding compound, this substance is readily soluble in all the ordinary solvents excepting light petroleum.

Bis-toluene-p-*sulphon*-m-*phenylenediamide*, produced by condensing its generators in pyridine solution, crystallises from dilute acetic acid or alcohol in white needles melting at 172°; it is hydrolysed by cold concentrated sulphuric acid.

Bis-o-*nitrotoluene*-p-*sulphon*-p-*phenylenediamide*, obtained by the method employed for preparing its isomerides, crystallises from acetone in pale yellow prisms melting above 250°; it readily dissolves in hot acetone, but is sparingly soluble in the other organic solvents. G. T. M.

Complex Cyclic Systems containing Nitrogen. By Oscar Hinsberg (*Annalen*, 1901, **319**, 257—286).—Systems of conjugated six-membered rings, arranged with their centres in a straight line, are indicated by the prefix "*lin*" (linear), those interlinked in such a manner that more than two of their centres never lie in the same straight line are denoted by the prefix "*ang*" (angular), whilst the double prefix "*lin-ang*" is employed for compounds exhibiting both forms of conjugation.

Lin-dihydronaphthaphenazine (dihydro-$\beta_1\beta_2$-naphthaphenazine), obtained from 2 : 3-dihydroxynaphthalene and *o*-phenylenediamine, readily yields its azine when oxidised with potassium dichromate and acetic acid; the reverse change is readily effected by the action of stannous chloride or alcoholic ammonium sulphide. The azine yields a compound with benzenesulphinic acid and reacts with aniline, giving rise to *anilino-$\beta_1\beta_2$-naphthaphenazine*, $NHPh\cdot C_{16}H_9N_2$, a change involving simultaneous addition of the amine and oxidation.

lin-ang-Dihydronaphthazine ($a_1\beta_1\beta_1'\beta_2'$-dihydronaphthazine), obtained from 2 : 3-dihydroxynaphthalene and 1 : 2-naphthylenediamine, readily yields its azine on oxidation with dichromate and acetic acid, the latter base melting at 246—247°, and not at 240° (Fischer and Albert, Abstr., 1896, i, 701).

lin-*Dihydronaphthazine* (*$\beta_1\beta_2\beta_1'\beta_2'$-dihydronaphthazine*), produced by heating together 2 : 3-dihydroxynaphthalene and 2 : 3-naphthylenediamine in a current of carbon dioxide at 180°, is obtained as a yellow, crystalline powder and does not melt below 300°. All attempts to oxidise this dihydro-base to the corresponding azine were fruitless.

Fluoflavine, formed from 2 : 3-dichloroquinoxaline and *o*-phenylenediamine has already been shown to be easily oxidised to quinoxalophenazine (Abstr., 1896, i, 394). The reverse change is very readily effected by the action of reducing agents, such as ammonium sulphide, stannous chloride, sulphurous acid, and quinol. The double azine is readily converted into chlorofluoflavine and phenylfluoflavylsulphone by the action of hydrochloric acid and benzenesulphinic acid respectively, the sulphone being oxidised by chromic acid mixture to the sulphone of the double azine.

lin-ang-*Naphthafluoflavine* (*aβ-naphthafluoflavine*) results from the condensation of 2 : 3-dichloroquinoxaline with 1 : 2-naphthylenediamine at 140—160°; it crystallises in yellow needles and melts above 300°.

lin-ang-*Quinoxalonaphthazine* (*quinoxalo-aβ-naphthazine*), obtained by oxidising the preceding compound, crystallises in blood-red leaflets and decomposes at 290°. The reverse change is effected by the ordinary reducing agents, excepting quinol in alcoholic solution; this azine is accordingly less reactive than quinoxalophenazine.

lin-ang-*Chloronaphthafluoflavine*, $C_{18}H_{11}N_4Cl$, produced by mixing the preceding double azine with concentrated hydrochloric acid, separates from glacial acetic acid in yellow needles and melts above 300°.

lin-*Naphthafluoflavine* (*$\beta_1\beta_2$-naphthafluoflavine*), prepared by melting together at 130—150° 2 : 3-dichloroquinoxalone and 2 : 3-naphthylenediamine, crystallises from glacial acetic acid in yellow needles and melts above 300°; it is sparingly soluble in alcohol or benzene and yields a potassium derivative on treatment with alcoholic potassium hydroxide. It is not possible to convert this substance into the corresponding double azine by oxidation with chromic acid.

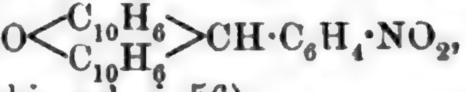
From these experimental results, the following conclusions are deduced. The stability of the azines and double azines diminishes as the number of linearly conjugated rings increases, the compounds of this type with five linearly arranged rings being incapable of existence; conversely, the stability of the dihydrogenised nitrogen compounds increases with the number of the linearly attached rings.

The *ang*-compounds are more stable than their *lin*-isomerides. The addition to a linear system of one or more rings angularly disposed increases its stability.

The remainder of the communication is devoted to a discussion of the application of these principles to other cases of conjugated ring systems. G. T. M.

Derivatives of Phenyl[pheno]naphthacridine. By Fritz Ullmann, N. A. Racovitza, and Melanie Rozenband (*Ber.*, 1902, **35**, 316—325. Compare Abstr., 1900, i, 360, 361, 689).—5-Phenyl-3-methylphenonaphthacridine (compare this vol., i, 55) yields a *hydrochloride* crystallising in yellow needles which are decomposed by water; the *platinichloride* is a yellow, crystalline, insoluble substance.

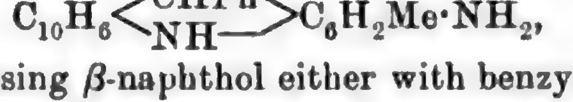
p-Nitrobenzylidene-*p*-toluidine behaves unlike its isomeride, *m*-nitrobenzylidene-*p*-toluidine, when condensed with β-naphthol, and yields chiefly *p*-nitrobenzylidene-β-dinaphthyloxide,



$O{<}\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}{>}CH\cdot C_6H_4\cdot NO_2$,

and only a trace of an acridine derivative (this vol., i, 56).

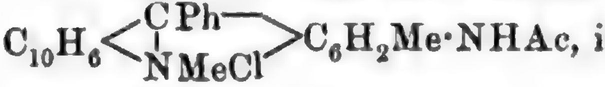
2-*Amino*-5-*phenyl*-3-*methyl*-5 : 12-*dihydrophenonaphthacridine*,



$$C_{10}H_6{<}\begin{matrix}CHPh\\NH\end{matrix}{>}C_6H_2Me\cdot NH_2,$$

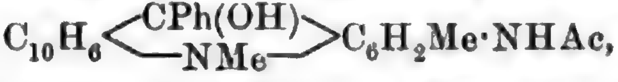
produced by condensing β-naphthol either with benzylidene-*m*-tolylenediamine or the corresponding tetra-aminoditolylphenylmethane, separates from aniline in white crystals melting indefinitely at 271°; on oxidation with ferric chloride, it yields the hydrochloride of the corresponding acridine (this vol., i, 56), this salt separating from dilute acetic acid in red leaflets. The acetyl derivative of 2-amino-3-methyl-5-phenylphenonaphthacridine, when treated with dimethyl sulphate in nitrobenzene solution, gives rise to the corresponding acridinium methyl sulphate, which separates in yellow crystals.

2-*Acetylamino*-5-*phenyl*-3-*methylphenonaphthacridinium methochloride*,



$C_{10}H_6{<}\begin{matrix}CPh\\|\\NMeCl\end{matrix}{>}C_6H_2Me\cdot NHAc$, is produced from the preceding salt by double decomposition with sodium chloride, and separates in orange-yellow crystals; the *platinichloride* and *dichromate* are yellow and red crystalline precipitates respectively.

2-*Acetylamino*-5-*phenyl*-3 : 5-*dimethylphenonaphthacridol*,



$$C_{10}H_6{<}\begin{matrix}CPh(OH)\\NMe\end{matrix}{>}C_6H_2Me\cdot NHAc,$$

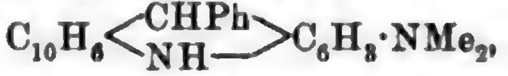
obtained by treating the methochloride with alcoholic ammonia, crystallises from xylene in pale pink coloured leaflets melting and decomposing at 210°.

2-*Amino*-5-*phenyl*-3-*methylphenonaphthacridinium methochloride*, resulting from the hydrolysis of the corresponding acetyl derivative, crystallises in red needles soluble in hot water. The corresponding *nitrate* is prepared by mixing 2-amino 5-phenyl-3-methylphenonaphthacridine with dimethyl sulphate in nitrobenzene solution, and treating the residue, after distillation, in steam with nitric acid; it separates in red crystals sparingly soluble in water; the *platinichloride* is an orange-coloured, crystalline substance; the *dichromate* is a dark-red insoluble powder.

G. T. M.

2-Alkylamino-5-phenylphenonaphthacridines. By Fritz Ullmann, Melanie Rozenband, Benno Mühlhauser, and E. Grether (*Ber.*, 1902, **35**, 326—340. Compare preceding abstract).—2-*Dimethyl*-

amino-5-phenyldihydrophenonaphthacridine,

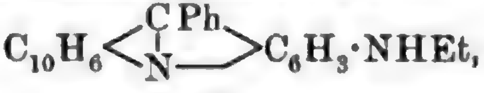


$$C_{10}H_6{<}\begin{matrix}CHPh\\NH\end{matrix}{>}C_6H_3{\cdot}NMe_2,$$

produced by condensing together a mixture of *m*-aminodimethylaniline, benzaldehyde, and β-naphthol, separates from benzene as an almost colourless, crystalline powder melting at 230°.

2-*Dimethylamino-5-phenylnaphthacridine* is obtained by oxidising the preceding compound either with atmospheric oxygen or ferric chloride; the base forms orange-yellow needles and melts at 216°; its *hydrochloride* crystallises from dilute acetic acid in brick-red needles; the *dichromate* is a red, insoluble powder.

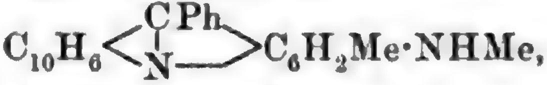
2-*Ethylamino-5-phenylphenonaphthacridine*,

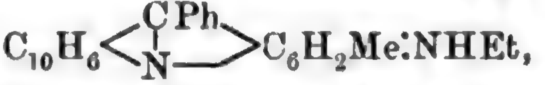


$$C_{10}H_6{<}\begin{matrix}CPh\\|\\N\end{matrix}{>}C_6H_3{\cdot}NHEt,$$

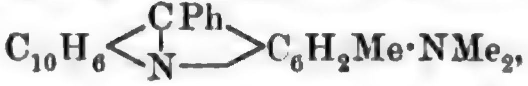
prepared from *m*-aminoethylaniline, separates in yellowish-brown crystals and melts at 220–221°.

2-*Methylamino-5-phenyl-3-methyldihydrophenonaphthacridine*, obtained by condensing 4-aminomethyl-*o*-toluidine with benzaldehyde and β-naphthol, is a white, crystalline powder melting at 247°, and dissolving in benzene to a solution exhibiting a blue fluorescence.

The corresponding *acridine* base,  $C_{10}H_6{<}\begin{matrix}CPh\\|\\N\end{matrix}{>}C_6H_2Me{\cdot}NHMe$, prepared from the preceding compound by the action of alcoholic ferric chloride, crystallises from benzene in yellow leaflets melting at 270°; its solutions are yellow and exhibit a green fluorescence; the *hydrochloride* forms orange-yellow needles sparingly soluble in boiling water.

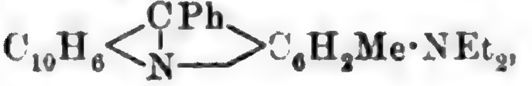
4-Aminoethyl-*o*-toluidine, when condensed in a similar manner, yields 2-*ethylamino-5-phenyl-3-methyldihydrophenonaphthacridine*, a pale yellow, crystalline powder melting at 227°, which, on oxidation, gives rise to the corresponding *acridine*,  $C_{10}H_6{<}\begin{matrix}CPh\\|\\N\end{matrix}{>}C_6H_2Me{\cdot}NHEt$, a base forming yellow needles and melting at 258°; the *hydrochloride* separates in lustrous, red needles; the *nitrate* is obtained in light red, lustrous leaflets sparingly soluble in water, but more so in alcohol.

2-*Dimethylamino-5-phenyl-3-methylphenonaphthacridine*,



$$C_{10}H_6{<}\begin{matrix}CPh\\|\\N\end{matrix}{>}C_6H_2Me{\cdot}NMe_2,$$

and its *dihydro*-compound, produced from aminodimethyl-*o*-toluidine by the condensation previously indicated, separate respectively in orange-red needles and white, crystalline granules, the corresponding melting points being 210° and 238°; the *hydrochloride* and the *nitrate* of the former base form lustrous, red needles and scarlet leaflets respectively.

4-*Nitrodiethyl-o-toluidine*, produced by nitrating diethyl-*o*-toluidine, is a reddish oil, boiling with slight decomposition at 295—297° under 727·5 mm. pressure; on reduction, it yields 4-*aminodiethyl-o-toluidine*, an oil boiling at 265—266° under 730 mm. pressure. The diamine, on condensation, gives rise to 2-*diethylamino-5-phenyl-3-methyldihydrophenonaphthacridine*, a substance obtained as a white, crystalline powder melting at 186°, and this in turn yields the *phenonaphthacridine*,  $C_{10}H_6{<}\begin{matrix}CPh\\|\\N\end{matrix}{>}C_6H_2Me{\cdot}NEt_2$, a base crystallising in yellow needles and melting at 200—201°, the *hydrobromide* of which separates from dilute alcohol in lustrous, red leaflets.

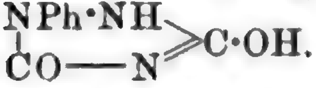
4-*Nitrobenzyl*-o-*toluidine*, prepared by heating 4-nitro-*o*-toluidine with benzyl chloride in nitrobenzene solution, crystallises from alcohol, benzene, or glacial acetic acid in yellow leaflets melting at 124°; on reduction, it gives rise to 4-*aminobenzyl*-o-*toluidine*, a diamine crystallising in colourless, silky needles and melting at 81°.

2-*Benzylamino*-5-*phenyl*-3-*methylphenonaphthacridine* results from the simultaneous condensation and oxidation of the preceding base with benzaldehyde and β-naphthol; it crystallises in pale yellow needles, melts at 302°, and is somewhat sparingly soluble in the organic solvents of low boiling point. The *hydrochloride* and *hydrobromide* of this acridine separate in thick, dark-red prisms or needles.

The hydrochlorides of the preceding acridine derivatives dye wool mordanted with tannic acid from a dilute acetic acid bath.

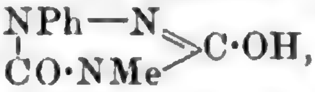
G. T. M.

Constitution of Phenylurazole. By S. F. Acree (*Ber.*, 1902, **35**, 553—562. Compare Pinner, Abstr., 1887, 1043; 1888, 687).—*Ethyl phenylsemicarbazidedicarboxylate*, $CO_2Et\cdot NPh\cdot NH\cdot CO\cdot NH\cdot CO_2Et$, obtained by the action of ethyl chlorocarbonate on phenylsemicarbazide, exists in two crystalline modifications melting at 172° and at 154°, and, when warmed with excess of sodium hydroxide, is converted into phenylurazole. A study of the properties of the latter substance indicate that it is probably 3-*hydroxy*-5-*keto*-1-*phenyl*-2:5-*dihydrotriazole*,



$\begin{array}{l}NPh\cdot NH\\ \vert \\ CO—N\end{array}>C\cdot OH$.

When titrated with sodium hydroxide, using phenolphthalein as indicator, it behaves as a strong monobasic acid. The *silver* derivative forms a white precipitate decomposing at 252° and soluble in ammonia; the *barium* derivative, $(C_8H_6O_2N_3)_2Ba,2H_2O$, crystallises in plates decomposing at 280—300°. When phenylurazole is warmed with methyl iodide and alcoholic potash, it is converted into Busch and Heinrichs' 3-hydroxy-5-keto-1-phenyl-2-methyl-2:5-dihydrotriazole (Abstr., 1900, i, 314) melting at 183° The same derivative is obtained when silver phenylurazole is boiled with alcoholic methyl iodide solution. It is a monobasic acid, yields a *silver* salt, $C_9H_8O_2N_3Ag$, and is not decomposed when evaporated to dryness with concentrated hydrochloric acid, hence the methyl group is presumably attached to nitrogen. The isomeric 3-*hydroxy*-5-*keto*-1-*phenyl*-4-*methyl*-4:5-*dihydrotriazole*,

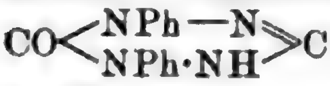


$\begin{array}{l}NPh—N\\ \vert \\ CO\cdot NMe\end{array}>C\cdot OH$,

may be obtained from phenylsemicarbazide and methylacetylcarbamide; it melts at 225°, gives a violet coloration with alcoholic ferric chloride, and yields mono-*sodium* and *silver* derivatives, the latter decomposing at 225°.

3-*Ethoxy*-5-*keto*-1-*phenyl*-2:5-*dihydrotriazole*, obtained by the action of ethyl iodide, in the cold, on a mixture of benzene and silver phenylurazole, is a crystalline solid melting at about 141° (?) and readily soluble in ether, benzene, or alcohol, but insoluble in alkalis. It is readily hydrolysed when warmed with alcoholic hydrochloric acid, and is isomeric with Wheeler's 5-hydroxy-3-ethoxy-1-phenyltriazole (Abstr., 1900, i, 563).

3-*Acetoxy-5-keto-1-phenyl-2 : 5-dihydrotriazole* is an oil, and is readily oxidised by acids or alkalis.

Diphenylurazine (Pinner, *loc. cit.*, and Heller, *Annalen*, 1891, **263**, 382) is a monobasic acid, yields a mono-silver salt, and from Rupe and Labhardt's researches (Abstr., 1899, i, 356) appears to have the formula  $CO\Big<\begin{matrix}NPh—N\\NPh\cdot NH\end{matrix}\Big>C\cdot OH$, and not the symmetrical constitution suggested by Pinner.

When warmed with alkali, it is not transformed into an isomeride melting at 231° as stated by Pinner.

J. J. S.

Synthesis of Aryl Leucauramines. By RICHARD MÖHLAU and M. HEINZE (*Ber.*, 1902, **35**, 358—375. Compare this vol., i, 63).—Arylamines readily react with tetramethyldiaminobenzhydrol, forming leucauramines with elimination of water, whilst aliphatic amines are not capable of interacting with the hydrol; similarly, arylamines and ordinary leucauramine yield substituted leucauramines and ammonia.

For the preparation of the benzhydrol, the authors recommend the oxidation of tetramethyldiaminodiphenylmethane hydrochloride in dilute aqueous solution by lead dioxide and acetic acid—a method which produces besides the hydrol a certain amount of hydrol-anhydride (see below). The reduction of Michler's ketone, by Michler and Dupertuis's method, also gives very good results.

Tetramethyldiaminodiphenylmethyl oxide, $O[CH(C_6H_4\cdot NMe_2)_2]_2$, is formed when the hydrol is heated at 100°, and is distinguished from the latter by its insolubility in ether; it crystallises in colourless, rhombic prisms, melting at 195°, and when heated with acids is reconverted into the hydrol.

Phenyl-leucauramine, $NHPh\cdot CH(C_6H_4\cdot NMe_2)_2$, prepared by heating molecular proportions of aniline and tetramethyldiaminobenzhydrol in alcoholic solution at 100°, or from aniline and leucauramine, or by reduction of phenylauramine by means of sodium amalgam, crystallises from benzene in colourless prisms melting at 154°. Although it dissolves in concentrated acids, forming a colourless solution, it is immediately decomposed by dilute acids into aniline and the benzhydrol. o-*Tolyl-leucauramine*, $C_6H_4Me\cdot NH\cdot CH(C_6H_4\cdot NMe_2)_2$, prepared in a similar manner from the benzhydrol and *o*-toluidine, forms colourless prisms melting at 133°; the p-*tolyl* derivative crystallises in colourless prisms melting at 150°, and unlike the ortho-derivative may be boiled with alcohol without undergoing decomposition. *m*-Toluidine does not react with the benzhydrol. m-*Xylyl-leucauramine*, $C_6H_3Me_2\cdot NH\cdot CH(C_6H_4\cdot NMe_2)_2$, prepared from *m*-xylidine and the benzhydrol, crystallises in colourless prisms melting at 147°.

Anilinoleucauramine, $NHPh\cdot NH\cdot CH(C_6H_4\cdot NMe_2)_2$, prepared from phenylhydrazine and the benzhydrol or from phenylhydrazine and leucauramine, forms colourless prisms melting at 116°. This substance could not be obtained by reduction of the phenylhydrazone of tetramethyldiaminobenzophenone (prepared by heating auramine hydrochloride and phenylhydrazine at 160°); with zinc dust and sodium hydroxide, the latter yielded *tetramethyldiaminodiphenylmethylimine*, $NH[CH(C_6H_4\cdot NMe_2)_2]_2$, which melts at 135°.

α-Naphthyl-leucauramine, $C_{10}H_7{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, prepared from α-naphthylamine and the benzhydrol, crystallises in colourless, prismatic needles melting at 182°; the *β-naphthyl* derivative forms colourless prisms melting at 191°.

o-*Nitrophenyl-leucauramine*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, prepared from *o*-nitroaniline and the benzhydrol, crystallises in golden-yellow, prismatic needles melting at 164°; the m-*nitro*-derivative in golden-yellow prisms melting at 152°; and the p-*nitro*-derivative in lemon-yellow prisms melting at 186°; the last-mentioned substance is far more stable towards boiling alcohol than the two former. p-*Ethoxyphenyl-leucauramine*, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, prepared from *p*-phenetidine and the benzhydrol, forms prisms melting at 159—160°.

Phenylene-p-*dileucauramine*, $C_6H_4[NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2]_2$, prepared by boiling *p*-phenylenediamine (1 mol.) and the benzhydrol (2 mols.) in alcoholic solution, crystallises in colourless prisms melting at 225°; the analogous *compound*, obtained by using *m*-phenylenediamine, melts at 247—248°, and is far more stable towards acids than the other leucauramines, yielding with dry hydrogen chloride a hydrochloride which forms colourless leaflets.

m-*Amino*-p-*tolyl-leucauramine*, $NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CH(C_6H_6{\cdot}NMe_2)_2$ [$Me : NH_2 : NH = 1 : 3 : 4$], prepared from tolylene-3:4-diamine and the benzhydrol, forms prismatic crystals melting at 165°. o-*Amino*-p-*tolyl-leucauramine*, $NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$ [$Me : NH_2 : NH = 1 : 2 : 4$], obtained by using tolylene-2 : 4-diamine, crystallises in colourless crystals melting at 209°.

Diphenylene-4 : 4′-*dileucauramine*, $C_{12}H_8[NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2]_2$, prepared from benzidine and the benzhydrol, crystallises in colourless prisms melting at 242—243°. 3 : 3′-*Dimethyldiphenylene*-4 : 4′-*dileucauramine*, $C_{12}H_6Me_2[NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2]_2$, forms colourless, lustrous prisms melting at 229—230°.

Dianisylene-4 : 4′-*dileucauramine*,

$$C_{12}H_6(OMe)_2[NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2]_2,$$

crystallises in colourless prisms with a silky lustre melting at 259—260°.

o-*Leucauraminobenzoic acid*, $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, prepared from *o*-aminobenzoic acid and the benzhydrol, crystallises in colourless prisms melting at 153°; the corresponding *p*-derivative forms prisms melting at 192—193°; its *sodium* salt crystallises in leaflets. *m*-Aminobenzoic acid does not react with the benzhydrol.

Carbamide readily condenses with the benzhydrol, yielding *carbonyldileucauramine*, $CO[NH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2]_2$, which crystallises in star-shaped aggregates of colourless prisms melting at 250—251 ; the hydrochloride forms leaflets. K. J. P. O.

New Reactions of Leucauramines. By Richard Möhlau, M. Heinze, and R. Zimmermann (*Ber.*, 1902, **35**, 375—383. Compare preceding abstract).—Although auramine is readily converted into leucauramine by reduction of an alcoholic solution with sodium amalgam (Graebe, Abstr., 1888, i, 158), reduction of the alkaline alcoholic solution with zinc dust leads to the formation of tetramethyldiaminodiphenylmethylimine (m. p. 185°, Weil, Abstr., 1894, i, 419). The latter compound is also formed when the benzhydrol is heated with leucauramine in alcoholic solution, or when leucauramine is heated at its melting point. By heating leucauramine and sulphur, together at 140°, tetramethyldiaminothiobenzophenone (m. p. 202°, Fehrmann, Abstr., 1888, i, 156, and Wallach, Abstr., 1891, i, 189) is produced. When hydrogen sulphide is passed into an alcoholic solution of leucauramine, *tetramethyldiaminodiphenylmethyl sulphide*, $S[CH(C_6H_4{\cdot}NMe_2)_2]_2$, is formed, crystallising in rhombic plates melting at 172°; it is also obtained when aryl-leucauramines are treated with hydrogen sulphide, and when leucauramine and aryl-leucauramines are acted on by ammonium sulphide, $(NH_4)_2S$. With ammonium polysulphide, $(NH_4)_2S_2$, the aryl-leucauramines yield *tetramethyldiaminodiphenylmethyl disulphide*, $S_2[CH(C_6H_4{\cdot}NMe_2)_2]_2$, which crystallises in star-like aggregates of prisms melting at 207°.

Carbon disulphide and leucauramine readily condense to the *leucauramine* salt of tetramethyldiaminodiphenylmethyldithiocarbamic acid, $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}NH{\cdot}CS{\cdot}S{\cdot}NH_3{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, which forms colourless crystals melting at 167°. When warmed with alcohol, ammonia is evolved, and the *tetramethyldiaminodiphenylmethyl ester* of tetramethyldiaminodiphenylmethyldithiocarbamic acid,

$$CH(C_6H_4{\cdot}NMe_2)_2{\cdot}NH{\cdot}CS_2{\cdot}CH(C_6H_4{\cdot}NMe_2)_2,$$

which crystallises in thin, colourless needles melting at 168°. When heated under pressure, carbon disulphide and leucauramine yield tetramethyldiaminodiphenylmethyl sulphide. The aryl-leucauramines and carbon disulphide give phenylthiocarbimide and tetramethyldiaminodiphenylmethyl disulphide.

Tetramethyldiaminothiobenzhydrol (D.R.-P., 58198) does not condense with aromatic bases, and readily breaks up into hydrogen sulphide and the sulphide previously described. K. J. P. O.

Action of Semicarbazide on Benzil. By HEINRICH BILTZ and THANKMAR ARND (*Ber.*, 1902, **35**, 344—347. Compare Posner, this vol., i, 82).—Benzilmonosemicarbazone is obtained, even at the ordinary temperature, on adding potassium acetate to an alcoholic solution of benzil and semicarbazide hydrochloride; it crystallises in colourless, octagonal plates and melts at 174—175°. The supposed isomeride of this compound indicated by Posner is in reality 5 : 6-diphenyl-3-oxy-1 : 2 : 4-triazine formerly described by Thiele and Stange.

Benzildisemicarbazone, $C_2Ph_2(N{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, prepared by boiling semicarbazide hydrochloride, benzil, and potassium acetate in dilute alcohol for 8 hours, crystallises from alcohol or pyridine in thin leaflets melting at 243—244°; it is accompanied by 5 : 6-diphenyloxytriazine, being separated from this substance by fractional crystallisation from alcohol.

Both these carbazones are readily hydrolysed by concentrated hydrochloric acid. G. T. M.

Action of Hypophosphorous Acid on Diazo-compounds. By JULIUS MAI (*Ber.*, 1902, **35**, 162—163).—The use of cuprous hydride in Sandmeyer's reaction was first tested, but it was found that diazo-salts were readily converted into hydrocarbons by the action of the hypophosphorous acid used in its preparation; for example, a 60 per cent. yield of diphenyl is obtained by the diazotisation of benzidine and subsequent treatment with hypophosphorous acid. R. H. P.

Esters of Nitronic Acids [*iso*Nitro-compounds] and Arylazoaldoximes. By EUGEN BAMBERGER (*Ber.*, 1902, 35, 54—66). —The name "nitronic acid" is suggested for substances containing the group $>C:NO \cdot OH$, instead of the name "*iso*nitro-compound" at present in use.

Methyl phenylazoethylidenenitronate $NPh:N \cdot CMe:NO_2Me$, is formed from diazomethane and phenylazonitroethane (nitroacetaldehyde phenylhydrazone, $NHPh \cdot N:CMe \cdot NO_2$, the product of the action of nitroethane and diazobenzene, V. Meyer, this Journ., 1875, 1202. The constitution follows from the fact that, with dilute hydrochloric acid, benzenediazonium chloride is formed, and that with an acetic acid solution of α-naphthylamine the ester gives an intense coloration, characteristic of the phenylazo-group. Further, this ester, which is very unstable, as are all derivatives of nitronic acids, is decomposed when heated with water into formaldehyde and an acidic substance which proved to be phenylazoacetaldoxime, $NPh:N \cdot CMe:NOH$ (compare Seidel, Abstr., 1892, 1417, and Nef, Abstr., 1895, i, 3, on the decomposition of ethyl fulminurate, &c.); the latter forms a monobenzoyl derivative and with dilute hydrochloric acid yields hydroxylamine, diazobenzene, and acetaldehyde (which is oxidised to acetic acid); further, it is produced by reduction of nitroacetaldehyde phenylhydrazone in alkaline solution to phenylhydrazoacetaldoxime, $NHPh \cdot NH \cdot CMe:NOH$, and subsequent oxidation of the latter by ferric chloride, and by the interaction of alkyl nitrites and acetaldehyde phenylhydrazone in the presence of sodium ethoxide, reactions which are generally applicable to the synthesis of arylazoaldoximes.

The arylazoaldoximes are all yellow, well crystallised substances, soluble in alkalis and easily reduced to arylhydrazoaldoximes. With concentrated hydrochloric acid, phenylazoacetaldoxime yields *p*-chlorophenylhydrazoacetaldoxime, $C_6H_4Cl \cdot N_2H_2 \cdot CMe:NOH$; this was also synthesised from *p*-chlorodiazobenzene and nitroethane, the nitroacetaldehyde *p*-chlorophenylhydrazone thus obtained yielding, on reduction, the hydrazoaldoxime.

The reaction of hydrochloric acid and phenylazoacetaldoxime is represented thus: there is first formed an additive product, a chlorohydrazoacetaldoxime, $NPhCl \cdot NH \cdot CMe:NOH$, which in the presence of hydrochloric acid undergoes an intramolecular transformation, the chlorine taking the place of the hydrogen atom in the para-position in the benzene nucleus relative to the nitrogen atom. *p*-Chlorophenylazoacetaldoxime, prepared by oxidation of the hydrazo-compound with hydrochloric acid, gives 2 : 4-dichlorophenylhydrazoacetaldoxime, and the azo-compound obtained from this with hydrochloric acid similarly yields 2 : 4 : 6-trichlorophenylhydrazoacetaldoxime. 2:4:6-Trichlorophenylazoacetaldoxime reacts with hydrogen chloride in ethereal solution, yielding 2 : 4 : 6-trichlorophenylhydrazoacetaldoxime, *s*-trichlorobenzene, acethydroxamic acid, and nitrogen; the chlorohydrazo-derivative first formed reacts with the excess of hydrogen chloride, giving chlorine and the hydrazo-compound; the chlorine thus set free converts part of the azo-compound into chloroacethydroxamic acid and trichlorodiazonium chloride; these substances respectively are converted into acethydroxamic acid and trichlorobenzene and nitrogen.

In the Griess reaction of diazonium salts with alcohol, the author sees an analogy with the decomposition of alkylphenylazoethylidenenitronate with water into an aldehyde and phenylazoacetaldoxime; the diazonium ether, $N⫶NPh\cdot OEt$, first formed, is, on the one hand, transformed into the diazo-ether, $NPh⁚N\cdot OEt$, which yields phenyl ethyl ether and nitrogen, on the other hand decomposed into acetaldehyde and phenylazohydride, $NPh⁚NH$, which is immediately converted into benzene and nitrogen. K. J. P. O.

Ester of Phenylazoethylidenenitronic Acid and Phenylazoacetaldoxime. By EUGEN BAMBERGER and JAC. GROB (*Ber.*, 1902, **35**, 67—82. Compare preceding abstract).—*Methyl phenylazoethylidenenitronate*, $N_2Ph⁚CMe⁚NO_2Me$, is prepared by adding diazomethane to an ethereal solution of nitroacetaldehyde phenylhydrazone, and crystallises in dark ruby-red, rhombic pyramids melting at 71·5—72°; in this reaction, there is also formed a small quantity of a substance crystallising in yellow needles melting at 95·5—96°. The ester is extremely unstable and decomposes rapidly into phenylazoacetaldoxime and formaldehyde; on reduction with stannous chloride, phenylhydrazoacetaldoxime is obtained.

Phenylazoacetaldoxime, $N_2Ph\cdot CMe⁚NOH$, is prepared by boiling the substance just described with water, and crystallises in orange-yellow, monoclinic needles melting at 117—118°, and readily soluble in alkalis. Concentrated sulphuric acid dissolves the oxime with a red coloration, which, on addition of water, becomes first blue and finally orange-yellow. When warmed with hydrochloric acid, it decomposes into acetaldehyde, benzenediazonium chloride, and hydroxylamine, the two former appearing respectively as acetic acid and phenol. *Benzoylphenylazoacetaldoxime*, $N_2Ph\cdot CMe⁚NOBz$, prepared by the Schotten-Baumann method, crystallises in pale yellow, flattened needles melting at 137—137·5°; the *phenylcarbamide* derivative,

$$N_2Ph\cdot CMe⁚NO\cdot CO\cdot NHPh,$$

prepared by the action of phenylcarbimide, crystallises in orange-red, lustrous needles melting at 123·5—124°.

Phenylhydrazoacetaldoxime, $N_2H_2Ph\cdot CMe⁚NOH$, is prepared by reducing phenylazoacetaldoxime by an alcoholic solution of ammonium sulphide, and crystallises in white needles or leaflets melting at 128°; the base is very readily oxidised to the azo-oxime,—an operation which is best effected by ferric chloride.

On treating phenylazoacetaldoxime with concentrated hydrochloric acid, it is immediately converted into p-*chlorophenylhydrazoacetaldoxime hydrochloride*, $C_6H_4Cl\cdot N_2H_2\cdot CMe⁚NOH,HCl$, which crystallises in needles melting and decomposing at 169°; the *base*, obtained from the hydrochloride, crystallises in white needles with a silky lustre melting and decomposing at 129°. p-*Chlorophenylazoacetaldoxime*, $C_6H_4Cl\cdot N_2\cdot CMe⁚NOH$, prepared from the hydrazo-compound by oxidation with ferric chloride or by the air in presence of water, crystallises in pale orange-yellow needles melting at 187—188°; the *benzoyl* derivative, prepared by the Schotten-Baumann method, crystallises in orange-red needles melting at 167—167·5°; the *phenylcarbamide* derivative forms orange-red prisms melting at 129—130°. When *p*-chlorophenylhydrazoacetaldoxime is oxidised with nitrous acid, p-*chlorophenylazoxyacetaldoxime*, $C_6H_4Cl\cdot N_2O\cdot CMe\colon NOH$, is formed, crystallising in very pale yellow needles melting at 101·5°.

On boiling *p*-chlorophenylazoacetaldoxime with dilute sulphuric acid, hydrolysis takes place with the formation of acetaldoxime and *p*-chlorobenzenediazonium sulphate; from the former, acetic acid and hydroxylamine are produced, and from the latter *p*-chlorobenzeneazoimide, *p*-chlorophenol, *p*-chloroaniline, and nitrogen.

When *p*-chlorophenylazoacetaldoxime in acetic acid solution is treated with α-naphthylamine and hydrochloric acid, p-*chlorobenzeneazo-α-naphthylamine*, $C_6H_4Cl\cdot N_2\cdot C_{10}H_6\cdot NH_2$, is formed; the latter was also prepared from a *p*-chlorobenzenediazonium salt and α-naphthylamine, and crystallises in brown, lustrous needles melting at 187·5—188°; the *hydrochloride* forms dark violet-red needles.

The synthesis of *p*-chlorophenylazoacetaldoxime was effected as follows. *Nitroacetaldehyde* p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot N_2H\colon CMeNO_2,$$

was prepared by adding a solution of *p*-chlorobenzenediazonium acetate to a solution of nitroethane in sodium hydroxide; it crystallises in orange-yellow, lustrous needles melting and decomposing at 126—127°. By the action of diazomethane, the last-mentioned substance is converted into *methyl* p-*chlorophenylazoethylidenenitronate*,

$$C_6H_4Cl\cdot N_2\cdot CMe\colon NO_2Me,$$

which crystallises in orange-red leaves with a bronze lustre and melts at 112—112·5°; it is converted by boiling with water into *p*-chlorophenylazoacetaldoxime (m. p. 187—188°) and formaldehyde. K. J. P. O.

Action of Hydrogen Chloride on Arylazoacetaldoximes. By EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1902, **35**, 82—91. Compare preceding abstracts).—2 : 4-*Dichlorophenylhydrazoacetaldoxime hydrochloride*, $C_6H_3Cl_2\cdot N_2H_2\cdot CMe\colon NOH,HCl$, is formed when *p*-chlorophenylazoacetaldoxime (*loc. cit.*) is warmed with concentrated hydrochloric acid, and crystallises in needles melting at 192—193°; the *base*, prepared from the hydrochloride by means of potassium acetate, forms white, lustrous needles melting and decomposing at 138°. On oxidation by air in presence of dilute sodium hydroxide, or by ferric chloride, 2 : 4-*dichlorophenylazoacetaldoxime*, $C_6H_3Cl_2\cdot N_2\cdot CMe\colon NOH$, is obtained, crystallising in yellowish-red needles, melting and decomposing at 207°; this substance was synthesised from *nitroacetaldehyde-2 : 4-dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot N_2H\colon CMe\cdot NO_2$, which was prepared by the action of 2 : 4-dichlorobenzenediazonium acetate on nitromethane and crystallises in orange-yellow, silky needles melting at 95·5°; with diazomethane, *methyl* 2 : 4-*dichlorophenylazoethylidenenitronate*, $C_6H_3Cl_2\cdot N_2\cdot CMe\colon NO_2Me$, is formed as brick-red or ruby-red needles melting and decomposing at 110—111°. To convert the ester into the azoaldoxime and formaldehyde, it is best to boil it with a concentrated solution of calcium chloride, as the temperature of boiling water is not sufficiently high to bring about the change. On reduction of the azoaldoxime, dissolved in acetone with zinc dust in the presence of ammonium chloride, the hydrazoacetaldoxime just described is formed.

2 : 4 : 6-*Trichlorophenylhydrazoacetaldoxime hydrochloride*,

$C_6H_2Cl_3\cdot N_2H_2\cdot CMe\colon NOH,HCl$,

formed by the action of dry hydrogen chloride on 2 : 4-dichlorophenylazoacetaldoxime dissolved in absolute ether, crystallises in white leaflets, and by treatment with a solution of potassium acetate is converted into the *base*, which crystallises in lustrous needles melting and decomposing at 156·5°. It is readily oxidised by ferric chloride to 2 : 4 : 6-*trichlorophenylazoacetaldoxime*, $C_6H_2Cl_3\cdot N_2\cdot CMe\colon NOH$, which crystallises in brilliant, orange-red needles, melting and decomposing at 185—186°; this substance was also synthesised from *nitroacetaldehyde* 2 : 4 : 6-*trichlorophenylhydrazone*, $C_6H_2Cl_3\cdot N_2H\colon CMe\cdot NO_2$, which is prepared from 2 : 4 : 6-trichlorobenzenediazonium acetate and nitroethane, and crystallises in golden-yellow needles or leaflets melting at 98°; the *sodium* salt crystallises well. With diazomethane, it yields *methyl* 2 : 4 : 6-*trichlorophenylazoethylidenenitronate*, $C_6H_2Cl_3\cdot N_2\cdot CMe\colon NO_2Me$, which crystallises in dark Bordeaux-red needles melting at 89—90°; on boiling with a concentrated solution of calcium chloride, it decomposes into formaldehyde and 2 : 4 : 6-trichlorophenylazoacetaldoxime. As already described (this vol., i, 246), the last-mentioned substance gives with hydrogen chloride the corresponding hydrazo-compound, acethydroxamic acid, and *s*-trichlorobenzene. K. J. P. O.

Supposed Isomerism of Diazothiosulphonates. By B. DYBOWSKI and ARTHUR HANTZSCH (*Ber.*, 1902, **35**, 268—271. Compare Troeger and Ewers, Abstr., 1901, i, 171).—Diazothiosulphonates do not exist in two isomeric modifications, as stated by Troeger and Ewers (*loc. cit.*); the second amorphous form is in reality a mixture of the diazosulphone (azosulphone) and sulphur produced by the decomposition of the original diazothiosulphonate, $N\colon NAr\cdot S\cdot SO_2Ph = ArN\colon N\cdot SO_2Ph + S$.

Naphthaleneazobenzenesulphone, $C_{10}H_7\cdot N_2\cdot SO_2Ph$, separates from a mixture of ether and light petroleum as yellowish-brown crystals decomposing at 96°. J. J. S.

Azo-dyes from Phenylmethylglycine. By JULIUS MAI [and, in part, with R. KAHN and WILHELM HEIMANN] (*Ber.*, 1902, **35**, 576—582). —Phenylmethylglycine, $NMePh\cdot CH_2\cdot CO_2H$, readily reacts with diazonium salts, yielding azo-dyes, which are characterised by their solubility and fastness to soap. Since a hydrochloric acid solution of the base readily decomposes, yielding carbon dioxide and dimethylaniline, it is necessary that the reaction shall be completed in the course of a very short time. The following compounds have been prepared:

Benzeneazophenylmethylglycine, $NPh\colon N\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CO_2H,HCl$, from benzenediazonium chloride.

The p-*sulphonic acid*, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CO_2H$, brownish-violet, fluorescent crystals; it yields a *sodium* salt which is remarkably hygroscopic. The corresponding *m*-compound forms brown-coloured crystals and its *hydrochloride* is decomposed by water. The p-*carboxylic acid*, $CO_2H\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CO_2H$, forms reddish-brown crystals.

Diphenylazophenylmethylglycine, $C_6H_4Ph\cdot N_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CO_2H$, from phenylmethylglycine and tetrazodiphenyl chloride, forms a dark brown precipitate.

Similar compounds with phenylglycine (Hausdörfer, Abstr., 1889, 1013) itself have been prepared.

Benzeneazophenylglycine, $NPh{:}N\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H$, golden, glistening crystals melting at 140° and insoluble in water. Its p-*sulphonic acid*, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H$, decomposes above 250°; the normal and acid sodium salts, the barium salt and hydrochloride were analysed.

Methyl Benzeneazophenylcarbamate, $NPh{:}N\cdot C_6H_4\cdot NH\cdot CO_2Me$, forms yellowish-red needles. J. J. S.

Discrimination between Basic and Acidic Functions in Proteid Solutions. By Hugo Schiff (*Annalen*, 1902, **319**, 287—303. Compare this vol., i, 85).—The amino-groups in egg-albumin, involved in the production of the biuret coloration, are destroyed by the action of nitrous acid, and are probably contained in complexes, such as $R\cdot CO\cdot NH_2$. Formaldehyde, on the other hand, reacting with proteids, biuret, and malonamide, gives rise to more soluble products which still furnish the biuret coloration; the nitrogen combining with the methylene group is, in all probability, present in residues of the type $R\cdot C(NH_2)\cdot CO_2H$. This hypothesis is supported by the fact that the proteids resemble the amino-carboxy-acids in becoming more acidic when their solutions are treated with formaldehyde, this reagent apparently severing the connection between the aminogen and carboxyl radicles, and allowing the acid functions of the latter to become manifest.

A solution of egg-albumin neutralised by *N*/10 potassium hydroxide solution in the presence of phenolphthalein is rendered acid by formaldehyde, and the amount of alkali required to restore neutrality indicates a molecular weight of 3281 for the proteid. Fish-gelatin behaves similarly, and its molecular weight is deduced to be 4680; in this case, the end point is clearly indicated by litmus as well as by phenolphthalein. The amount of decomposition which the proteid molecule undergoes on hydrolysis can be ascertained by this reaction. The quantity of alkali required to neutralise the acidity produced by formaldehyde in a solution of fish gelatin after boiling for several hours with potassium hydroxide solution is 45 times as great as in the case of the undecomposed proteid.

The following salts of aminoamides give the biuret reaction and develop a yellow coloration with a nickel salt in the presence of potassium hydroxide. *a-Aminopropionamide hydrobromide*, $NH_2\cdot CO\cdot CHMe\cdot NH_2,HBr$, forms a syrupy mass which slowly crystallises. *a-Amino*iso*butyramide hydrobromide*, $NH_2\cdot CO\cdot CMe_2\cdot NH_2,HBr$, separates from dilute methyl alcohol in crystals, stable in the atmosphere, which melt and decompose at 210—220°. *a-Amino*iso*valeramide hydrobromide*, $NH_2\cdot CO\cdot CHPr^{\beta}\cdot NH_2,HBr$, is a crystalline substance decomposing at 200° (compare Schiff, Abstr., 1896, i, 284, 632). G. T. M.

Estimation of Sulphur in Proteids. By Thomas B. Osborne (*Zeit. anal. Chem.*, 1902, **41**, 25—35; from *Studies Research Lab. Connecticut Exper. Stat.*, 1900, 443—471).—The total sulphur was estimated by fusing the proteid with sodium peroxide and weighing as barium sulphate. The loosely combined sulphur was estimated by Schulz's method (Abstr., 1898, i, 502), which consists in cohobating the substance with sodium hydroxide, lead acetate, and metallic zinc (to prevent oxidation) for several hours, and ascertaining the amount of sulphur converted into lead sulphide. In another method, the zinc was omitted and the mixture was heated in an autoclave at 135—165° in an atmosphere free from oxygen. Except vicilin, phaseolin, and conglutin, all the proteids examined showed a constant percentage of total sulphur, and, omitting phaseolin and casein, they contain from $\frac{1}{3}$ to $\frac{2}{3}$ of their sulphur in the loosely combined condition. The author has previously given reasons for assuming that the molecular weights of the proteids approximate to 15,000 (*J. Amer. Chem. Soc.*, 1899, **21**, 486). If, for such of the proteids as can be obtained in crystals, and the constancy of composition of which is a criterion of purity, the simplest empirical formula be multiplied by the number which will give a molecular weight nearest to 15,000, the total sulphur will be found to range from 2 to 11 atoms. In those proteids which contain only 2 atoms of sulphur, almost exactly one-half of it is loosely combined. Proteids with a larger number of sulphur atoms in the molecule yield less than half their total sulphur when digested with sodium hydroxide. Mörner and Embden have found cystin and cystein in a variety of proteids, and Mörner has discovered another sulphuretted complex which yields lead sulphide on digestion with alkaline lead solution. It is well known that only half the sulphur of cystin and cystein can be removed as lead sulphide by Schulz's method. The suggestion is therefore made that cystin or cystein is a constituent of only those proteids which are comparatively rich in sulphur.

Casein forms a marked exception; of the 0·8 per cent. of total sulphur, only 0·1 can be obtained as lead sulphide. M. J. S.

Estimation of Iodic and Hydriodic Acids formed in the Iodination of Proteids. By C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1901, **34**, 194—206. Compare following abstract).—The amounts of iodic and hydriodic acid, produced when proteids are warmed with water and iodine for definite periods of time have been estimated and the results expressed in the form of curves. The proteids investigated were vitellin, crystallised egg-albumin, and "Casein Hammarsten." The whole process appears to be termolecular. J. J. S.

Formation of Iodic Acid in the Iodination of Crystallised Egg-albumin. By C. H. L. SCHMIDT (*Zeit. physiol. Chem.*, 1901, **34**, 55—65). —When a solution of crystallised egg-albumin is boiled for a short time with iodine, oxidation accompanied by the formation of hydrogen iodide occurs, and at the same time amino-groups are eliminated from the molecule in the form of ammonium iodate and iodide. Free hydriodic acid can only exist in the presence of an iodide and iodate within certain limits; if these are exceeded, reduction of the iodate begins. This accounts for the fact that the amount of iodate present in the iodinated proteid solution never exceeds a certain small maximum. The formation of iodate by the action of iodine on concentrated proteid solutions at the ordinary temperature is a characteristic of basic proteids. Carbamide, arginine, and guanidine-α-aminovaleric acid yield iodic acid. Aspartic acid does not. J. J. S.

Oxidation of Nitrogenous Substances. By W. Falta (*Ber.*, 1902, **35**, 294—296).—A reply to Jolles (this vol., i, 86. Compare Abstr., 1901, ii, 705). W. A. D.

Proteid-dissolving Enzyme in Malt. By E. Ehrich (*Bied. Centr.*, 1901, **30**, 857; from *Der Bierbrauer*, 1901, 4).—Malt is shown to contain an enzyme which dissolves proteids. The enzyme is very active in many malts, less active in others. N. H. J. M.

Emulsin. By G. Heut (*Arch. Pharm.*, 1901, **239**, 581—589).—The hydrolysing action of certain lichens on amygdalin and other glucosides was studied by Bourquelot's method (Abstr., 1894, ii. 63) and Hérissey (*Recherches sur l'émulsine, Lons-le-Saunier*, 1899). *Polyporus Clusianus, Cladonia delicata* and *C. digitata, Imbricaria saxatilis* and *Parmelia tenella* exerted this action on amygdalin; *Xanthoria parietina* did not; *Peltigera horizontalis* did if it had grown on a tree, not when it had grown on the ground. *Parmelia obscura* hydrolysed amygdalin readily when it had grown on a fence; the variety *virella*, which had grown on an Italian poplar, had but little action.

Hérissey was unable to ascertain whether pepsin digested emulsin in the presence of dilute hydrochloric acid or not, because in a blank experiment without pepsin the acid alone deprived the emulsin of its power to liberate glucose from amygdalin. The author finds that ½—1 per cent. malic acid certainly weakens, but does not destroy, the hydrolysing action of emulsin on amygdalin, but that if 1 per cent. of pepsin is added no sugar is formed. Evidently the pepsin does digest and destroy the emulsin. C. F. B.

Superoxydases. By Robert W. Raudnitz (*Zeit. Biol.*, 1901, **42**, 91—106).—Fresh milk decomposes hydrogen peroxide with the formation of free oxygen; this catalytic action is lost when the milk is boiled, and is attributed to a ferment termed a peroxydase. Thiocyanates have an inhibitory influence on this action, and this is due to the production of hydrocyanic acid. The decomposition of hydrogen peroxide by blood is mainly due to hæmoglobin. When this substance is recrystallised many times, it has the same catalytic property, this is also possessed by methæmoglobin and hæmatin, but not by hæmatoporphyrin; the property is therefore probably due to the constituent of hæmoglobin which contains iron. W. D. H.

Action of Trypsin on Gelatin. By Friedrich Reich-Herzberge (*Zeit. physiol. Chem.*, 1901, **34**, 119—121).—Kühne stated that gelatin under the influence of trypsin yields neither leucine nor glycine. Certainly tryptic digestion does not lead to any profound decomposition of gelatin, but there is always a small yield of leucine. W. D. H.

Organic Chemistry.

Linking of Carbon Atoms in the Paraffin Series. By Sima M. Losanitsch (*Bull. Soc. Sci. Bucuresci-România*, 1901, 353—396).—The author develops a method for calculating the number of possible isomerides of the paraffins, and gives the numbers in a table for the isomerides from CH_4 to $C_{16}H_{34}$.

A nomenclature is also suggested so as to indicate the number of carbon atoms, the nature, number, and sequence of the side-chains, and the position of the side-chains. J. McC.

Action of Potassium Hydride on Ethyl Iodide and Methyl Chloride. Formation of Ethane and Methane. By Henri Moissan (*Compt. rend.*, 1902, **134**, 389—392).—When ethyl iodide is heated with potassium hydride in sealed tubes at 180—200°, ethane is formed, together with potassium iodide. Methyl chloride and potassium hydride under the same conditions yield methane. A small quantity of hydrogen is liberated in both cases, but there is no liberation of carbon or iodine or chlorine. C. H. B.

Decomposition of Acetylene during its Combustion. By Fernand Gaud (*Compt. rend.*, 1902, **134**, 175—177).—The incrustation of carbon which forms round the orifices of acetylene burners is due to the decomposition of polymerides of this hydrocarbon. Since the polymerisation takes place only at temperatures above 100°, it follows that this change is due to the preliminary heating of the gas in the burner. An ordinary Manchester acetylene burner, when supplied with pure acetylene under a pressure sufficient to give a full flame, is only slightly coated with carbon after 12—13 hours, and maintains its efficiency even after 100 hours' use. When, however, the flame is turned down, the slow stream of gas becomes considerably heated in passing through the burner, polymerisation occurs, and a rapid incrustation is produced. G. T. M.

Study of the Acetylene Hydrocarbons: Synthesis of Acetylenoid Ketones and their Hydrolysis by Alkali Hydroxides. New Method of Synthesising β-Diketones. By Charles Moureu and Raymond Delange (*Ann. Chim. Phys.*, 1902, [vii], **25**, 239—268).—A *résumé* of work already published (compare Abstr., 1900, i, 397; 1901, i, 14, 352, 359, 581, and this vol., i, 164). G. T. M.

Presence of *n*-Butyl Alcohol in Fusel Oil from Grain. By Oskar Emmerling (*Ber.*, 1902, **35**, 694—695).—Ten litres of the fusel oil from grain yielded, on fractionation, 15 grams of a product boiling at 114—118°; this substance was impure *n*-butyl alcohol, which was purified by successive conversion into iodide and acetate, 2·5 grams of the pure alcohol being ultimately obtained. This compound is most conveniently prepared from glycerol by fermentation with cow-dung; the fermenting agent when dried preserves its power for many years.

G. T. M.

Some Derivatives of Primary Nitro*iso*pentane. By THÉOPHILE MOUSSET (*Bull. Acad. roy. Belg.*, 1901, 622—656).—The author has studied the condensation of primary nitro*iso*pentane with aldehydes; the action on it of sodium and halogens, of piperidylmethyl alcohol, and of reducing agents. The compound can condense either with 1 or with 2 mols. of aldehyde. With 1 mol. of formaldehyde it yields the *β-nitroisohexyl alcohol*, $OH\cdot CH_2\cdot CH(NO_2)\cdot CH_2\cdot CHMe_2$, a colourless liquid with a disagreeable odour and bitter taste, which boils at 141° under 32 mm. pressure, has a sp. gr. 1·060 at 13°, and is insoluble in water, but soluble in ether or alcohol. It forms a *sodium* salt, and on reduction with aluminium amalgam yields the corresponding *amino-isohexyl alcohol*, a colourless liquid which boils at 198—200° under 768 mm. pressure, has a sp. gr. 0·9173 at 13°, and yields a crystalline *platinichloride*. The amine forms a crystalline *dibenzoyl* derivative which melts at 124—125°; with ethyl oxalate, it yields the compound $C_2O_2[NH\cdot CH(CH_2\cdot OH)\cdot CH_2\cdot CHMe_2]_2$, which crystallises in pure white needles melting at 99—100°, and with picrolonic acid it forms a yellow salt which decomposes at about 245—247°. With phenylthiocarbimide, it gives a non-crystallisable substance. *a-Chloro-β-nitroisohexane*, formed by the action of phosphorus pentachloride on nitro*iso*hexyl alcohol, is a very mobile, faintly greenish-coloured liquid, which boils at 209—210° under atmospheric pressure and has a sp. gr. 1·090 at 18°. The *nitroisohexyl acetate* is a yellowish liquid which boils at 147° under 40 mm. pressure, and has a sp. gr. 1·059 at 13°. *a-Amino-β-isohexyl alcohol* is a colourless liquid which boils at 198—200°, and has a sp. gr. 0·890 at 17°. It forms a crystalline *platinichloride*, a crystalline *dibenzoyl* derivative which melts at 128°, and also a crystallisable salt with picrolonic acid which decomposes at about 240—243°. With 2 mols. of formaldehyde, primary nitro*iso*pentane yields a heptylene glycol, $CHMe_2\cdot CH_2\cdot C(NO_2)(CH_2\cdot OH)_2$, which crystallises in white needles and melts at 98°. With acetaldehyde, nitro*iso*pentane forms nitro-γ-*iso*heptanol, $CHMe_2\cdot CH_2\cdot CH(NO_2)\cdot CHMe\cdot OH$, a colourless liquid which boils at 132° under 30 mm. pressure and has a sp. gr. 1·020 at 13°. With a mixture of formaldehyde and acetaldehyde, nitro*iso*pentane yields the *octylene glycol*,

$$CHMe_2\cdot CH_2\cdot C(NO_2)(CH_2\cdot OH)\cdot CHMe\cdot OH.$$

By passing chlorine into an aqueous solution of the sodium derivative of nitro*iso*pentane, *chloronitroisopentane*, $CHMe_2\cdot CH_2\cdot CHCl\cdot NO_2$, is produced; it is a colourless, mobile liquid which boils at 178° under 750 mm. pressure, has a sp. gr. 1·177 at 13°, and is insoluble in water but soluble in alkalis, ether, or alcohol. *Bromonitroisopentane*, obtained in a similar manner, boils at 119—120° under 80 mm. pressure, and has a sp. gr. 1·453 at 13°. With formaldehyde, it yields *β-bromo-β-nitro-isohexyl alcohol*, $CHMe_2\cdot CH_2\cdot CBr(NO_2)\cdot CH_2\cdot OH$, a brownish-coloured liquid which boils at 159—161° under 55 mm. pressure, and has a sp. gr. 1·461 at 13°.

With piperidylmethyl alcohol, nitro*iso*pentane yields the compound

$CHMe_2 \cdot CH_2 \cdot C(NO_2)(CH_2 \cdot C_5NH_{10})_2$, a white, crystalline substance which melts at 40°.

The author has also succeeded in obtaining methyl*iso*butylamine by the direct reduction of primary nitro*iso*pentane with tin and hydrochloric acid. A. F.

A Glycol Isomeric with Pinacone. By ADOLF FRANKE (*Monatsh.*, 1901, **22**, 1067—1072).—Diacetone alcohol (see Abstr., 1900, ii, 395) is reduced by aluminium amalgam to *β-methylpentane-βδ-diol*, $OH \cdot CHMe \cdot CH_2 \cdot CMe_2 \cdot OH$, which boils at 190—194° under 740 mm. pressure, does not solidify at − 20°, and has a sp. gr. 0·9231 at 22°. The mol. weight was found in two determinations to be 117·7 and 119·5. The *diacetate* distils at 95° under 12 mm. pressure. When boiled with dilute sulphuric acid, the glycol does not yield pinacoline. This new *β*-glycol is isomeric with pinacone, which must therefore be an *α*-glycol. G. Y.

Hydroxy*iso*propylhypophosphorous Acid. By CH. MARIE (*Compt. rend.*, 1902, **134**, 286—288. Compare Abstr., 1901, i, 635).—Hydroxy*iso*propylhypophosphorous acid (H_3PO_2,C_3H_6O) is best purified by fusing it under dry ether and then decanting the liquid; it forms a lustrous, radiating, solid mass which melts at 45° (compare *loc. cit.*). At 110—120°, or when boiled with acids, it decomposes into hypophosphorous acid and acetone; it is readily oxidised by mercuric chloride or ferric salts to the acid H_3PO_3,C_3H_6O, and when boiled with acetone yields the acid $H_3PO_2,2C_3H_6O$. The *cobalt* salt crystallises in rose-coloured, silky tufts with $4H_2O$, and is blue when anhydrous; the *nickel* salt crystallises with $4H_2O$, and is green, or pale yellow when anhydrous; the *copper* salt is pale blue, and crystallises with H_2O; when heated in carbon dioxide at 100°, it decomposes into copper, and hydroxy*iso*propylphosphorous, and hydroxy*iso*propylhypophosphorous acids. It is similarly decomposed by boiling water, but in the presence of air, copper hydroxy*iso*propylphosphite is formed. The *silver* salt is anhydrous, and in solution soon darkens and deposits silver. The *methyl* and *ethyl* esters obtained from the silver salt are viscous liquids; the former has a sp. gr. 1·212 and n_D 1·462 at 16°. K. J. P. O.

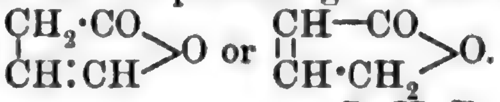
Glycero-arsenic Acid. By VICTOR AUGER (*Compt. rend.*, 1902, **134**, 238—240).—When arsenic acid and glycerol are heated together, glycero-arsenic acids are formed, with elimination of one or two mol. proportions of water as the case may be. If calcium dihydrogen arsenate is heated with glycerol, a calcium glycero-arsenate is obtained as a white, deliquescent solid. Both the acids and the calcium salt are, however, at once decomposed by water, and hence cannot be formed in solution (compare Pagel, Abstr., 1901, i, 498). C. H. B.

New Synthesis of Formic Acid. By HENRI MOISSAN (*Compt. rend.*, 1902, **134**, 261—264. Compare this vol., ii, 136).—A rapid stream of pure dry carbon dioxide is passed over crystalline potassium hydride which has been volatilised along a glass tube. The potassium hydride quickly changes in appearance, and much heat is developed.

To avoid a deposition of carbon, which takes place if the temperature rises to any extent, the tube must be cooled. The substance formed from potassium hydride and carbon dioxide proved to be potassium formate.

Carbon monoxide and potassium hydride react but slowly, even at 210°. If a mixture of hydrogen (1 vol.) and carbon monoxide (2 vols.) is heated in contact with potassium, a fairly rapid absorption of the gases by the metal takes place; at the end of the reaction, the metal has become replaced by a mixture of carbon and crystalline needles, which are potassium formate. K. J. P. O.

Vinylacetic Acid. By Fritz Fichter and Ferdinand Sonneborn (*Ber.*, 1902, **35**, 938—943).—The impure vinylacetic acid previously obtained (Abstr., 1899, i, 255) can be purified from *iso*crotonic acid, since sodium vinylacetate is much less soluble in alcohol than sodium crotonate. The pure acid boils at 163°, or at 71° under 12—14 mm. pressure, has a sp. gr. 1·013 at 15°/15°, n_D 1·42572 at 15°, and a conductivity $K = 0·0051$. The *calcium* salt crystallises, with H_2O, in yellow, lustrous needles, the *barium* salt in small, lustrous, felted needles, and the *sodium* salt in lustrous laminæ. When treated with mineral acids, vinylacetic acid yields crotonic acid. The formula of the acid is proved to be $CH_2:CH\cdot CH_2\cdot CO_2H$, as the substance, when treated with bromine in carbon bisulphide solution, forms *βγ-dibromobutyric acid*, which is a crystalline compound melting at 49—50°, and when treated with water yields β-hydroxybutyrolactone. *β-Hydroxybutyrolactone*, when treated with baryta water, yields the barium salt of βγ-dihydroxybutyric acid, and when distilled under reduced pressure gives rise to an oily, unsaturated *butenelactone*, either



$\begin{matrix}CH_2\cdot CO\\ CH:CH\end{matrix}{>}O$ or $\begin{matrix}CH-CO\\ \| \\ CH\cdot CH_2\end{matrix}{>}O$.

R. H. P.

Preparation of γδ-Unsaturated Monobasic Acids. By A. A. Solonina (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 734—739).—The author has further studied the methylhexenoic acid of the composition $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CO_2H$, already prepared by Barbier (*Bull. Soc. Chim.*, 1887, [ii], 47, 701) and by Léser (Abstr., 1899, i, 414), which he has obtained by the action of ethyl sodiomalonate on the additive compound of hydrogen bromide and isoprene. The acid has the sp. gr. 0·9864 at 0°/0° and n_D 1·45041 at 17°; the molecular refraction (Lorenz and Lorentz formula) is 34·91, the number calculated from the formula being 35·93. The *silver*, *calcium* ($+2H_2O$), *barium* ($+3H_2O$), and *lead* ($+6H_2O$) salts were prepared as well as the methyl and ethyl esters. The last-named compound forms, with nitrosyl chloride, a *substance* melting at 75° and having the probable constitution $CMe_2Cl\cdot C(NOH)\cdot CH_2\cdot CH_2\cdot CO_2Et$.

The action of ethyl sodiomalonate on the additive compound of diethylallene with hydrogen bromide yields a diethyl ester,

$$CEt_2:CH\cdot CH_2\cdot CH(CO_2Et)_2;$$

on heating the corresponding acid, it evolves carbon dioxide and acetic acid, the residue consisting of an *acid*, $CEt_2:CH\cdot CH_2\cdot CH_2\cdot CO_2H$, which boils at 232—236° and has the sp. gr. 0·9589 at 0°/0° and 0·9459 at 15°/0°. It decolorises 1 per cent. potassium permanganate solution and becomes viscous when cooled in a mixture of ether and solid carbon dioxide. Its *silver* salt, which is white and amorphous, is sparingly soluble in water and readily decolorises permanganate solution.

T. H. P.

Solid Acids of Olive Oil. By D. Holde (*Chem. Centr.*, 1902, i, 177—178; from *Mitt. Techn. Vers-A. Berlin*, **19**, 115—117. Compare Abstr., 1901, i, 577).—The results of an examination of the solid acids of olive oil by fractional precipitation with magnesium acetate by Heintz's method, together with determinations of the melting points and mol. weights of the separate fractions and comparison with two artificial mixtures of stearic acid (1 mol.), melting at 69°, and palmitic acid (1 mol.) melting at 62·1°, show that the acids obtained from the oil do not consist of stearic and palmitic acids in these proportions. The mol. weights of the various fractions were all found to correspond with the formula $C_{17}H_{34}O_2$. The acids are therefore derived from a glyceride of the formula $C_3H_5(C_{17}H_{33}O_2)_2{\cdot}C_{18}H_{33}O_2$, and not from oleopalmitostearin.

E. W. W.

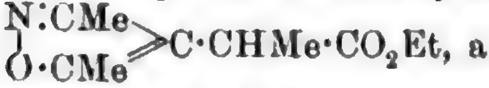
Formation of Lactic Acid from Pentoses by the Action of Potassium Hydroxide. By K. Katsuyama (*Ber.*, 1902, **35**, 669—671).—The statement of Araki (*Zeit. physiol. Chem.*, **19**, 463) that arabinose yields lactic acid when heated with sodium hydroxide is confirmed, and it is shown that xylose also yields lactic acid when heated with potassium hydroxide.

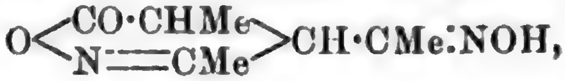
T. M. L.

Trimethylpentanolic Acid. By Karl Michel and Karl Spitzauer (*Monatsh.*, 1901, **22**, 1109—1118).—$\alpha\alpha\gamma$-Trimethyl-β-pentanolic acid, $CHMe_2{\cdot}CH(OH){\cdot}CMe_2{\cdot}CO_2H$, is best obtained by preparing the ethyl ester by the condensation of *iso*butaldehyde and ethyl bromo*iso*butyrate by the action of zinc (Reformatzky's method). On hydrolysis of the ester by potassium hydroxide, part of the acid decomposes to *iso*butyric acid and *iso*butaldehyde; the latter, in presence of potassium hydroxide, undergoes the normal condensation to octyleneglycol and trimethylpentanolic acid. As the acid decomposes most easily at the moment of formation, the reaction proceeds until the whole of the *iso*butaldehyde is converted into octoglycol and *iso*butyric acid (see Lieben, Abstr., 1901, i, 449).

G. Y.

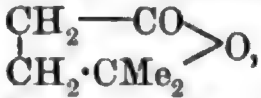
Action of Alkyl Halogen-substituted Propionates on Sodioacetylacetone. By Fr. March (*Compt. rend.*, 1902, **134**, 179—181. Compare Abstr., 1901, i, 312, 596).—*Ethyl $\beta\beta$-diacetyl-α-methylpropionate*, $CHAc_2{\cdot}CHMe{\cdot}CO_2Et$, obtained by the interaction of ethyl α-bromopropionate on sodioacetylacetone at 120—140°, boils at 149—151° and at 128—130° under pressures of 33 and 10 mm. respectively, and has a sp. gr. 1·067 at 15°; it is insoluble in water but dissolves in ether or alcohol, develops a deep red coloration with ferric chloride, and is decomposed by aqueous and alcoholic sodium hydroxide solutions into sodium lævulate and ethyl lævulate respectively, sodium acetate being a product common to both hydrolyses.

When treated with hydroxylamine hydrochloride and potassium carbonate, the ester yields its *dioxime*, $C_{10}H_{18}O_4N_2$, melting at 133°; this compound is accompanied by *ethyl dimethyloxazole-a-propionate*,  $\begin{array}{l}N{:}CMe\\ \vert\\ O\cdot CMe\end{array}>C\cdot CHMe\cdot CO_2Et$, an oil boiling at 143—145° under 21 mm. pressure. The corresponding acid, $C_8H_{11}O_3N$, crystallises in colourless needles and melts at 106°; it is soluble in ether or water; its green *copper* salt melts at 254—255°.

If, in preparing the dioxime, the boiling is continued for 24 hours, this substance undergoes condensation with elimination of alcohol, giving rise to the *compound*  $O<\begin{array}{l}CO\cdot CHMe\\ N{=\!=}CMe\end{array}>CH\cdot CMe{:}NOH$, which melts at 203—204° and develops a deep red coloration with alcoholic ferric chloride. Semicarbazide reacts with ethyl ββ-diacetyl-a-methylpropionate to form the compound $C_{12}H_{22}O_4N_6,\frac{1}{2}H_2O$; this product, which is sparingly soluble in the ordinary solvents, when crystallised from ethyl acetate, melts at 207—208°, and then has the composition $C_{12}H_{22}O_4N_6,\frac{1}{2}CH_3\cdot CO_2Et$.

Ethyl γγ-diacetylbutyrate, $CHAc_2\cdot CH_2\cdot CH_2\cdot CO_2Et$, produced by the interaction of ethyl β-chloropropionate and sodioacetylacetone, boils at 154—155° under 15 mm. pressure, and develops a red coloration with ferric chloride; its *copper* derivative, $Cu_2(C_{10}H_{15}O_4)_2$, melts at 209°. G. T. M.

Action of Aluminium Chloride on certain Anhydrides in Chloroform Solution. By Marcel Desfontaines (*Compt. rend.*, 1902, **134**, 293—296).—Following the observations of Tiemann (Abstr., 1897, i, 199) on the action of sulphuric acid on camphoric acid, when carbon monoxide is eliminated and a γ-lactone, terpenylic acid, formed, and the experiments of Blanc (*Bull. Soc. Chim.*, 1901, [iii], **25**, 68) on the formation of *iso*lauronolic acid by the action of aluminium chloride on camphoric anhydride, the action of the latter reagent has been tried on the anhydrides of dicarboxylic acids, in which one of the carboxyl groups is tertiary.

aa-Dimethylglutaric anhydride, dissolved in chloroform, reacts vigorously with aluminium chloride; carbon monoxide is evolved and *iso*hexolactone,  $\begin{array}{l}CH_2—CO\\ \vert\\ CH_2\cdot CMe_2\end{array}>O$, formed; the identity of the latter was established by conversion into ethyl γ-bromo*iso*hexoate. At the same time, aa-dimethylglutaric and pyroterebic acids are produced.

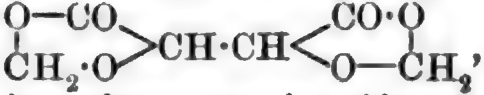
Dimethylsuccinic anhydride and aluminium chloride yield carbon monoxide and dimethylacrylic acid, dimethylsuccinic acid being formed at the same time. K. J. P. O.

Action of Ethyltrioxymethylene Chloride on Ethyl Sodiomalonate. By G. H. Coops (*Rec. Trav. Chim.*, 1901, **20**, 430—434).—By the action of hydrogen chloride on formaldehyde, ethyltrioxymethylene chloride, $OEt\cdot CH_2\cdot O\cdot CH_2\cdot O\cdot CH_2Cl$, is formed, among other substances. On adding this mixture to ethyl sodiomalonate, a product is obtained which, on hydrolysis with potassium hydroxide, yields *β-isomalic acid*, $OH\cdot CH_2\cdot CH(CO_2H)_2$, of which the *lead* and *calcium* salts were prepared. K. J. P. O.

A Chlorogalactonic (Chlorotetrahydroxyhexoic) Acid. By OTTO RUFF and ARTHUR FRANZ (*Ber.*, 1902, **35**, 943—948).—When galactonolactone is treated with acetyl choride, a *monochlorotriacetyl* derivative, $C_{12}H_{15}O_8Cl$, is obtained; this crystallises in rhombic prisms, which sinter at 95—96° and melt at 98° (corr.), and has $[\alpha]_D$ $-22{\cdot}41°$ at 20°. When treated with alcoholic ammonia, it yields the *amide* of chlorogalactonic acid $C_6H_{12}O_5NCl$, which crystallises in silky needles melting at 194·5° (corr.) and has $[\alpha]_D$ $+71{\cdot}43°$ at 20°. The action of liquid ammonia yields insoluble *substances* of undetermined composition decomposing at 227° and 240—250° respectively. The *anilide* of chlorotriacetylgalactonic acid, $C_{12}H_{15}O_8Cl,NH_2Ph$, crystallises in silky needles, which melt and decompose at 187·5°. The *piperidide* of chlorogalactonic acid, $C_{11}H_{20}O_5NCl$, is deliquescent and crystallises with 1 mol. of piperidine in colourless prisms. The authors find the specific rotation of galactonolactone to be $[\alpha]_D$ $-77{\cdot}61°$ at 20°, altering in three days to $-67{\cdot}89°$; the melting point is 134—136° (corr.) (compare Tollens and Schnelle, Abstr., 1892, 1432).

R. H. P.

Influence of Ammonium Paramolybdate on the Specific Rotatory Power of Sodium Hydrogen Tartrate. By HERMANN ITZIG (*Ber.*, 1902, **35**, 690—692. Compare Rosenheim and Itzig, Abstr., 1900, i, 272; Klason and Köhler, this vol., i, 75).—A maximum specific rotatory power is reached in solutions of sodium hydrogen tartrate when ammonium paramolybdate is added in the ratio of 0·692 of molybdate to 0·576 of tartrate. T. M. L.

Compound of Tartaric Acid with Formaldehyde. By WILHELM STERNBERG (*Chem. Centr.*, 1902, i, 299; from *Pharm. Zeit.*, 1901, **46**, 1003—1004. Compare Abstr., 1901, i, 120).—*Diformal tartrate* or *dimethylene tartrate*,  $\begin{array}{l}O-CO\\ |\\ CH_2\cdot O\end{array}\!>CH\cdot CH<\!\begin{array}{l}CO\cdot O\\ \quad\;\;|\\ O-CH_2\end{array}$, prepared by dissolving trioxymethylene in molten tartaric acid and adding sulphuric acid to the viscous syrup which is formed, crystallises in colourless needles, melts at 120°, boils at 296°, and may be sublimed; it is easily soluble in alcohol, acetone, ethyl acetate, or chloroform, is decomposed by dilute sodium carbonate solution even at a blood heat, and more quickly by alkali hydroxides, but is not so readily attacked by acids. This compound is not the methyl ester of methylenetartaric acid, since repeated evaporation of its aqueous solution is sufficient to decompose it with liberation of tartaric acid; the behaviour of malonic and succinic acids with formaldehyde also justifies this conclusion.

Attempts to prepare methylenetartaric acid by digesting tartaric acid with formalin and hydrochloric acid failed. E. W. W.

Action of Formaldehyde on Citric Acid. By WILHELM STERNBERG (*Chem. Centr.*, 1902, i, 299—300; from *Pharm. Zeit.*, 1901, **46**, 1004. Compare Abstr., 1901, i, 120, and 1902, i, 76).—*Methylene-*

citric acid, $C_7H_8O_7$, prepared by heating citric acid with paraformaldehyde at 140—160°, or by evaporating formalin and hydrochloric acid with citric acid, crystallises from water in prisms grouped together in star-like aggregates, melts and decomposes at 205°, is readily soluble in hot, but only slightly in cold, water, is not decomposed by boiling with water or dilute acids, but is attacked by alkali hydroxides or carbonates. The silver salt is a white, amorphous powder, and is soluble in 1500 parts of water.
E. W. W.

Characterisation of Pseudo-acids by Conductivity Determinations of Aqueous-Alcoholic Solutions. By ARTHUR HANTZSCH and E. VOEGELEN (*Ber.*, 1902, **35**, 1001—1009).—This is an additional method for the characterisation of pseudo-acids, and depends on the different course of dissociation of true and pseudo-acids in aqueous-alcoholic solution.

The compound, which is thought to be a pseudo-acid, is dissolved in alcohol of different strengths, usually containing 25, 40, 50, 75, and 100 per cent. of alcohol by volume. The electrical conductivities of these solutions are measured, and the numbers compared with numbers obtained from solutions of the same strength, but containing a true acid, the dissociation constant of which, in pure water, is practically the same as that of the supposed pseudo-acid. If the conductivity numbers for the solutions of the true acid decrease much more rapidly than the numbers for the solutions of the pseudo-acid as the strength of the alcohol is increased, then the compound must be a pseudo-acid. The following examples illustrate the relationship of the numbers obtained for a true and pseudo-acid. Violuric acid (pseudo-acid), $K = 0·0027$. Lævulic acid (true acid), $K = 0·0024$:

Per cent. alcohol ...	0	25	40	50	75	100
Violuric acid $\mu 64$ ...	14·5	6·53	4·13	2·91	0·90	0·23
Lævulic acid $\mu 64$ ...	13·85	4·65	2·35	1·49	0·32	—
Nitroacetone $\mu 128$...	12·40	6·36	—	2·74	0·74	—
Acetic acid $\mu 128$ ...	16·99	6·12	—	1·93	—	—

Numerous other examples are given.

It does not necessarily follow because the numbers for the supposed pseudo-acid solutions decrease as rapidly as, or more rapidly than, those of a similar true acid, that the compound is not a pseudo-acid, for example, nitroacetophenone and succinic acid:

Alcohol per cent.	0	25	50	75
Nitroacetophenone $\mu 256$..	41·1	10·0	4·0	1·2
Succinic acid $\mu 256$.........	43·9	15·8	5·3	1·4

J. J. S.

Paraldol and Viscid Acetaldol. By ALEXANDER KARL NOWAK (*Monatsh.*, 1901, **22**, 1140—1145).—Molecular weight determinations by freezing point and boiling point methods show that paraldol and the viscid acetaldol have the same molecular weight, which in dilute solutions approaches the unimolecular, in concentrated solutions the bimolecular, value.

Paraldol sublimes unchanged at 73° under 1—2 mm. pressure. The viscid aldol distils at 73° under 16 mm. pressure and condenses partly as the crystalline paraldol and to a small extent as the mobile aldol.

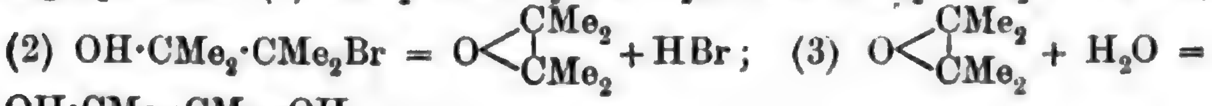
G. Y.

Alkoxides of Bromal. By Emilio Gabutti (*L'Orosi*, 1901, **24** 364—366).—*Bromal glycolate*, $C_2H_4[O\cdot CH(OH)\cdot CBr_3]_2$, prepared by the action of bromal (2 mols.) on ethylene glycol (1 mol.), is a dense, colourless oil having a pungent odour; it boils at 145—150° and is soluble in alcohol or ether.

Bromalglycol monoacetate, $CBr_3\cdot CH(OH)\cdot O\cdot CH_2\cdot CH_2\cdot OAc$, obtained from bromal and ethylene glycol monoacetate, is a colourless oil of pungent odour, which boils at 168—169° and dissolves in ether or alcohol.

T. H. P.

Formation of Aldehydes and Ketones from Haloid Derivatives of Ethylene Hydrocarbons. By K. Krassusky (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 791—808).—When βγ-dimethyl-β-butylene is mixed with water and lead oxide and the liquid shaken from time to time, pinacone, $OH\cdot CMe_2\cdot CMe_2\cdot OH$, is formed to the extent of 57 per cent. of the theoretical yield, together with a smaller quantity of tetramethylethylene oxide. The reactions are expressed by the following equations: (1) $CMe_2Br\cdot CMe_2Br + H_2O = OH\cdot CMe_2\cdot CMe_2Br + HBr$;



$$(2)\ OH\cdot CMe_2\cdot CMe_2Br = O\!<\!\begin{matrix}CMe_2\\ |\\ CMe_2\end{matrix} + HBr;\quad (3)\ O\!<\!\begin{matrix}CMe_2\\ |\\ CMe_2\end{matrix} + H_2O =$$

$OH\cdot CMe_2\cdot CMe_2\cdot OH$.

The action of water on β-methyl-β-butylene bromide in presence of lead oxide takes place much less readily than in the preceding case and requires constant shaking of the reacting mixture. The first product of the reaction may be regarded as $OH\cdot CMe_2\cdot CHMeBr$, which is resolved into hydrogen bromide and β-methyl-β-butylene oxide, 15 per cent. of the theoretical yield of the latter being obtained. Some of the β-methyl-β-butylene oxide takes up water, giving the glycol, $OH\cdot CMe_2\cdot CHMe\cdot OH$, which is formed in about 20 per cent. yield.

At the ordinary temperature, water acts very slowly on *iso*butylene bromide in presence of lead oxide, but at 50° the action proceeds somewhat more rapidly, giving 38 per cent. of the theoretical yield of *iso*butylene glycol; no *iso*butylene oxide is obtained, as at the temperature at which the reaction is carried out this compound wholly combines with water.

Propylene and ethylene bromides are very slowly attacked by water in presence of lead oxide at 50°.

T. H. P.

β-Diketones. III. By Georges Leser (*Bull. Soc. Chim.*, 1902, [iii], **27**, 64—71. Compare Abstr., 1901, i, 278, 430).—In the present paper, the author describes a number of diketones which he has prepared for the purpose of comparing their properties with those of the diketo*cyclo*hexanes previously studied, and with the view of obtaining some light on the tautomeric relationships. Acetylmethylheptanone (*decane-ζθ-dione*), obtained by the action of sodium on a mixture of methylheptanone and ethyl acetate, boils at 117—119° under 20 mm. pressure, and gives a blood-red coloration with ferric chloride. Its copper salt crystallises from alcohol in needles of a fine blue colour. The mol. refraction of the free diketone is 50·9 (calculated for the di-enolic form, 50·4). With hydroxylamine, it yields only one *iso*oxazole, boiling at 126—128° under 27 mm. pressure. By the action of methyl iodide on the sodium salt of the diketone, acetyldimethylheptanone is obtained, which boils at 131—132° under 20 mm. pressure and gives a clear red coloration with ferric chloride; the mol. refraction is 53·8 (calculated for the keto-enolic form, 54·0). It yields an *iso*oxazole which boils at 133—135° under 20 mm. pressure.

α-Octene-εη-dione, obtained by the condensation of allylacetone with ethyl acetate in presence of sodium, is a liquid with the odour of garlic, boils at 87—89° under 16 mm. pressure, and has the mol. refraction 41·2 (calculated for the di-enolic form, 40·8). *ζ-Methyl-α-octene-εη-dione*, boils at 97—99° under 10 mm. pressure, and has the mol. refraction 44·2 (calculated for the keto-enolic form, 44·4). Its *iso*oxazole boils at 112—114° under 20 mm. pressure.

Acetylmethylheptenone (β-methyl-β-nonene-ζθ-dione) (compare Abstr., 1899, i, 110) has the mol. refraction 50·9 (calculated for the di-enolic form, 50·0). *Methylacetylmethylheptenone* is a liquid which boils at 127—128° under 10 mm. pressure; it is insoluble in alkalis, and gives a clear red coloration with ferric chloride. Its mol. refraction is 53·65 (calculated for the keto-enolic form, 53·66). It yields an *iso*oxazole boiling at 127—129° under 8 mm. pressure.

Three substances are obtained by the action of sulphuric acid on acetylmethylheptenone: (1) 2-acetyl-1 : 1-dimethyl*cyclo*hexanone-3; (2) a hydration product having the constitution

$$OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot COMe,$$

which boils at 153—154° under 12 mm. pressure; (3) a dehydration product of this substance which boils at 237—238° under normal pressure. On boiling 2-acetyl-1 : 1-dimethyl*cyclo*hexanone-3 with alkalis and condensing the dimethyl*cyclo*hexanone formed with ethyl acetate in presence of sodium, *4-acetyl-*1 : 1*-dimethyl*cyclo*hexanone-*3 is obtained isomeric with the first, the acetyl having migrated to position 4; this substance boils at 122—123° under 18 mm. pressure and yields a copper salt which crystallises in greyish-green, silky needles. The diketone is soluble in alkalis and gives a blood-red coloration with ferric chloride (compare Abstr., 1899, i, 743). The mol. refraction of 2-acetyl-1 : 1-dimethyl*cyclo*hexanone is 47·3 (calculated for the keto-enolic form, 47·3), and that of the 4-acetyl-1 : 1-dimethyl*cyclo*hexanone-3 is 48·8 (calculated for the di-enolic form, 48·3).

3-*iso*Butyryl-1-methyl*cyclo*pentanone-4, which was obtained by Baeyer and Oehler (Abstr., 1896, i, 247), has the mol. refraction 48·4 (calculated for the di-enolic form, 48·3). Its methyl derivative boils at 108—109° under 8 mm. pressure and has the mol. refraction 51·13 (calculated for the diketonic form, 51·00). It yields a monoxime which melts at 94°.

Propionylacetophenone, obtained by Beyer and Claisen (compare Abstr., 1887, 943), has the mol. refraction 54·4 (calculated for the di-enolic form, 51·7). Its methyl derivative boils at 165—166° under 10 mm. pressure and has the mol. refraction 57·45 (calculated for the keto-enolic form, 55·36).

The author draws the following conclusions. The mol. refraction of the aromatic β-diketones deviates in an abnormal manner from the value calculated by means of the atomic increments. The non-aromatic β-diketones containing an ethylene linking have a mol. refraction which is appreciably higher than the value calculated for the di-enolic form. The saturated β-diketones, cyclic or open-chained, containing the groups CH and CH_2 respectively between the two carbonyls, have a mol. refraction equal to that calculated for the di-enolic form. Diketones containing no labile hydrogen have the true diketonic form. Unsubstituted, open-chain diketones can yield both dioximes and *iso*oxazoles; those containing only one labile hydrogen atom yield only *iso*oxazoles. Cyclic β-diketones containing one carbonyl group in the nucleus and one in the side chain yield only dioximes, and when the only labile hydrogen atom which they possess is substituted, they yield only monoximes. A. F.

Isomeric Acetylhalogen Derivatives of Sugars and the Synthesis of Glucosides. By Emil Fischer and E. Frankland Armstrong (*Ber.*, 1902, **35**, 833—843. Compare Abstr., 1901, i, 257, 671).—In the preparation of acetylchlorodextroses and the corresponding bromo-compounds, it is not advisable to leave the penta-acetyldextrose in contact with the halogen acid for more than 1½ hours. If liquid hydrogen bromide is allowed to remain in contact with penta-acetyldextrose for 8 days, the product is *triacetyldibromodextrose*, $C_{12}H_{16}O_7Br_2$, obtained by the replacement of two acetate groups by two bromine atoms. It melts at 176·5° (corr.), may be crystallised from ethyl acetate, and is readily soluble in chloroform or acetone. It reduces Fehling's solution but slightly, and on treatment with methyl alcohol and silver carbonate yields *triacetylmethylglucoside bromohydrin*, $C_{13}H_{19}O_8Br$, crystallising in needles and melting at 126—127° (corr.). This does not reduce Fehling's solution until after hydrolysis with mineral acids, and is readily soluble in benzene, chloroform, or ethyl acetate. The compound described by Skraup and Kreman (Abstr., 1901, i, 506) is identical with β-tetra-acetylchlorogalactose. Both crystallise from ether in long prisms melting at 82—83°, or from light petroleum in needles melting at 76—77°.

β-Tetra-acetylbromogalactose, $C_{14}H_{19}O_9Br$, obtained by the action of liquid hydrogen bromide on penta-acetylgalactose, crystallises from light petroleum in small prisms melting at 82—83° and has $[\alpha]_D$ $+236·4°$ at 20°. Penta-acetylgalactose itself has $[\alpha]_D$ $+7·48°$. *Tetra-acetyl-β-phenolgalactoside*, $C_{20}H_{24}O_{10}$, crystallises from dilute alcohol or from benzene in stout prisms melting at 123—124° (corr.), and has $[\alpha]_D$ $-25·77°$ at 20°. When hydrolysed, it yields *β-phenolgalactoside* melting at 139—141° (corr.) and having $[\alpha]_D$ $-39·38°$ at 20°. This galactoside is not hydrolysed by yeast extract, but, like all β-glucosides, is decomposed by emulsin.

Hepta-acetylchloromaltose melts at 66—68°.

Octa-acetyllactose, as obtained by Schmoeger's method (Abstr., 1892, 948), appears to be a mixture; by repeated crystallisation from benzene, the melting point has been raised to 106°. On treatment with liquid hydrogen chloride, it is converted into a mixture of two *hepta-acetylchlorolactoses*, which may be separated by repeated crystallisation from light petroleum. The one crystallises from this medium in prisms melting at 57—59° and has $[\alpha]_D$ +76·2° at 20°. The isomeride, which is insoluble in light petroleum, crystallises in minute prisms melting at 118—120° and has $[\alpha]_D$ +73·5° at 20°.

Tetra-acetylmannitol dichlorohydrin, $C_{14}H_{20}O_8Cl_2$, formed when liquid hydrogen chloride is left in contact with hexa-acetylmannitol for 14 days, melts at 214° (corr.) and distils at a higher temperature with only slight decomposition. J. J. S.

Isolation of Ketoses. By CARL NEUBERG (*Ber.*, 1902, **35**, 959—966).—Secondary asymmetric hydrazines of the type $R\cdot NPh\cdot NH_2$ can oxidise the group $-CO\cdot CH_2\cdot OH$, but not the group $-CH(OH)\cdot CHO$, to the group $-CO\cdot CHO$; they therefore yield osazones with ketoses, but hydrazones with aldoses. Phenylmethylhydrazine was found to be best suited for the purpose, and condenses readily in acetic acid solution with ketoses, forming osazones which mostly crystallise readily from alcohol.

d-*Fructosephenylmethylosazone*, from lævulose, crystallises in long, slender, bright yellow crystals, melts at 158—160°, and could not be obtained from dextrose, mannose, or glucosamine.

d-*Fructosephenylbenzylosazone* crystallises in small, felted needles melting at 190°, and d-*fructosediphenylosazone* is a similar compound melting at 167°.

d-*Arabinoketosephenylmethylosazone* crystallises in orange-red needles which soften at 169° and melt and decompose at 172°.

Dihydroxyacetonephenylmethylosazone, obtained from the syrup given by the action of bromine on lead glycerate, crystallises in yellowish needles which melt and evolve gas at 127—130°.

Sorbosephenylmethylosazone is an oil.

The following example will show how ketoses may be separated from aldoses: a mixture of mannose and lævulose, obtained by the oxidation of *d*-mannitol, when treated with an alcoholic solution of phenylmethylhydrazine, deposits mannosephenylmethylhydrazone, and the filtered solution, when acidified with acetic acid and warmed, yields *d*-fructosephenylmethylosazone.

Dextrosephenylmethylhydrazone crystallises from alcohol in long, striated plates and melts at 130°. R. H. P.

Rotatory Power of Sucrose; its Variation with Temperature and with the Wave-length of the Light. By HENRI PELLAT (*Zeit. Ver. deut. Zuckerind.*, 1902, **552**, 1—3).—Replies to the criticisms of Schönrock on the author's work on this subject (Abstr., 1901, i, 672). T. H. P.

Density of Sucrose in Aqueous Solutions. By A. DEMICHEL (*Ann. Chim. anal.*, 1902, 7, 49—52).—As the result of a mathematical investigation, the author concludes that the supposed *liquid* sucrose, having a density of 1·55625 at 15°, does not exist. The figure is only the result of a calculation by a formula the application of which is no longer legitimate when the liquid has become supersaturated. L. DE K.

Amino-alcohols containing C_4 and C_5. By RENÉ TORDOIR (*Bull. Acad. roy. Belg.*, 1901, 695—702).—The author communicates the results of a study of the two compounds, *aβ-butanolamine* [*a-amino-*sec.*butyl alcohol*], $CH_3·CH_2·CH(OH)·CH_2·NH_2$, and β-aminodiethylcarbinol, $CH_3·CH_2·CH(OH)·CH(NH_2)·CH_3$. The former is obtained by the reduction of the corresponding nitro-compound, the reduction being best effected by means of aluminium amalgam; it is a colourless liquid, having a disagreeable odour of mice and a sharp taste, boils at 172° under 755 mm. pressure, has the sp. gr. 0·927 at 17° and n_D 1·4772, corresponding with a mol. refraction of 27·11 (calculated, 26·23). It is hygroscopic, and dissolves readily in water with rise of temperature. With benzoyl chloride, it yields a *dibenzoyl* derivative, $OBz·CHEt·CH_2·NHBz$, which melts at 107°. With picrolonic acid, the butanolamine forms a salt which crystallises in yellow, silky needles, decomposes at about 230°, and is very insoluble in water. Phenylthiocarbimide readily combines with the butanolamine, yielding a *thiocarbamide*,

$$NHPh·CS·NH·CH_2·CHEt·OH,$$

which crystallises from alcohol in small prisms melting at 102°. *Butanolamine oxalate* is a white, amorphous salt which melts at 193°. The *picrate* is a yellow, crystalline salt which decomposes at about 130°. With ethyl oxalate, butanolamine forms a *dihydroxybutyloxamide*, $C_2O_2(NH·CH_2·CHEt·OH)_2$, which crystallises from alcohol in scales melting at 198°.

Bi-secondary normal βγ-pentanolamine [*β-aminodiethylcarbinol*], obtained by the reduction of bi-secondary normal βγ-nitropentanol by means of aluminium amalgam, is a colourless liquid with a disagreeable taste and odour, which boils at 174° under 760 mm. pressure, has a sp. gr. 0·911 at 17°, n_D 1·4458, and mol. refraction 30·11 (calculated, 30·07); it is only slightly soluble in water. Its *dibenzoyl* derivative crystallises in scales, insoluble in water but soluble in alcohol or ether, and melts at 122°; the *picrolonate* crystallises in yellow, silky needles, which melt almost without decomposition at 215° (compare Jänecke, Abstr., 1899, i, 476).

Attention is further drawn to the fact that the boiling points of the two amino-alcohols described above are sensibly the same, showing that the introduction of the methyl group does not appreciably affect the volatility. A. F.

Amino-alcohols containing C_4 and C_5. By PAUL STIÉNON (*Bull. Acad. roy. Belg.*, 1901, 703—708).—*aβ-Butanolamine* [*β-aminobutyl alcohol*], $CH_3·CH_2·CH(NH_2)·CH_2·OH$, obtained by the reduction of the corresponding nitro-compound, is a liquid which boils at 172—174° under the ordinary pressure. With oxalic acid, it yields a white, amorphous oxalate which melts at 176°.

n-*βγ-Pentanolamine* [*γ-aminomethylpropylcarbinol*],

$$CH_3·CH_2·CH(NH_2)·CHMe·OH.$$

obtained by the reduction of the corresponding nitro-compound, is a colourless liquid which boils at 174° under 765 mm. pressure; it has a sp. gr. 0·906 at 18°, and is very slightly soluble in water but readily so in alcohol. With oxalic acid, it yields an acid and a normal salt, the former melting at 204°, the latter at 166°.

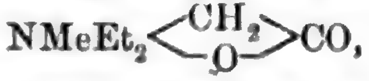
The replacement of a hydrogen atom in one of the CH_2 groups of ethanolamine (b. p. 171°) by ethyl has no effect on the boiling point, whilst the replacement of the hydrogen by methyl lowers the boiling point about 10°. A. F.

Derivatives of Glucosamine. By E. Roux (*Compt. rend.*, 1902, **134**, 291—293. Compare Abstr., 1901, i, 372).—On dissolving recently precipitated cupric hydroxide in a 10 per cent. aqueous solution of glucosamine, a blue solution is obtained, from which the *compound* $C_6H_{11}O_5NCu_2$ separates in rectangular plates of a clear blue colour. *Glucosamine picrate* crystallises in chrome-yellow, slender needles melting at 137°. *Glucosamine platinichloride* crystallises in pale yellow prisms melting at 116—118°.

When glucosamine is treated with boiling acetyl chloride, the *hydrochloride* of penta-acetylglucosamine is obtained as a mass of slender needles, which melt at 170° and readily volatilise. With acetic anhydride, glucosamine yields a *hexa-acetyl* derivative, which crystallises in small, hygroscopic leaflets melting at 70° and boiling at about 250°. *Benzylideneglucosamine*, $C_6H_{13}O_5N{:}CHPh$, prepared from benzaldehyde and glucosamine, crystallises in long, slender needles melting at 162—163° and decomposed by water. *Glucosaminecarbamide*, $C_6H_{14}O_5N{\cdot}CO{\cdot}NH_2$, prepared from glucosamine sulphate and potassium cyanate, forms needles, extremely soluble in water, which melt at 149° and have $[\alpha]_D$ $-12{\cdot}5°$. This substance does not reduce Fehling's solution, is hydrolysed by barium hydroxide forming carbon dioxide, ammonia, and glucosamine, with sodium hypobromite gives oxalic acid and the whole of the nitrogen in the form of gas, and with mercuric oxide or mercuric nitrate yields soluble compounds.

Glucosamine and phenylcarbimide in solution in pyridine yield a *phenylcarbamide*, $C_6H_{14}O_5N{\cdot}CO{\cdot}NHPh$, which crystallises in short needles melting at 174°, and does not evolve nitrogen when treated with sodium hypobromite. With excess of phenylcarbimide, a *pentaphenylcarbamic phenylcarbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_8O_5(CO{\cdot}NHPh)_5$, is obtained; it crystallises in microscopic needles melting and decomposing at 305°, and is not attacked by boiling acids or alkalis. K. J. P. O.

Betaines. By Richard Willstätter (*Ber.*, 1902, **35**, 584—620).—The betaines are termed *α*, *β*, *γ*, &c., according to the position of the amino-group. The prefixes also indicate the alkyl and acyl groups present; for example, *γ*-trimethylbutyrobetaine. The acetylbetaines are, for brevity, simply termed betaines, for example, methyldiethylbetaine,



$NMeEt_2{<}\genfrac{}{}{0pt}{}{CH_2}{O}{>}CO$,

The intramolecular reaction between methyl dimethylaminoacetate and betaine is a reversible one, below 135° both compounds are stable, between 135° and 293° the betaine is the stable form, but above 293° it is incapable of existence. The esters of other tertiary α-amino-acids cannot be transformed into betaines in a similar manner; when heated, they yield decomposition products of betaines, namely, tertiary amines. The esters of β- and γ-amino-acids in many cases yield betaines, or their decomposition products, when heated; for example, methyl dimethyl-β-aminopropionate and methyl dimethyl-γ-aminobutyrate. Methyl dimethylaminoformate may be heated considerably above its boiling point without undergoing decomposition.

The transformation of betaines into esters of amino-acids occurs in the case of all α-betaines, but not with the β- and γ-compounds.

When the betaine contains different alkyl groups, it is always the methyl group which passes to the carboxylic group (compare Lossen, *Annalen*, 1876, **181**, 377; Lawson and Collie, Trans., 1888, **53**, 625; Collie and Schryver, *ibid.*, 1890, **57**, 767).

Brühl's statement (this Journal, 1875, 1020; 1876, i, 698) that when triethylglycine is distilled a considerable portion passes over unchanged is incorrect; it gives an almost theoretical yield of ethyl diethylaminoacetate, together with a little triethylamine.

It is thought probable that although amino-acids may have the ammonium constitution (Walker, Proc., 1894, 94, and Sakurai, *ibid.*, 90), yet when they volatilise, it is in the form of the free acid containing a carboxylic group. In no case, however, have two desmotropic modifications been obtained.

Methyl dimethylaminoacetate, $NMe_2{\cdot}CH_2{\cdot}CO_2Me$, is a volatile oil boiling at 135° (corr.) or at 51—52° under 30 mm. pressure; it does not yield precipitates with platinic chloride or picric acid, and is usually accompanied by *dimethylaminoacetyldimethylamide*,

$$NMe_2{\cdot}CH_2{\cdot}CO{\cdot}NMe_2,$$

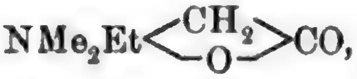
which distils at 99—100° under 34 mm. pressure, and further yields a crystalline *aurichloride*. The *methiodide* of the ester, $C_6H_{14}O_2NI$, crystallises from alcohol in colourless needles melting at 153·5—154·5°, or from acetone in long prisms.

Betaine melts and decomposes at 293°; the aurichloride melts at 209°, Fischer (*Ber.*, 1894, **27**, 165) gives 230—235°; the platinichloride (Jahns, Abstr., 1893, ii, 485; Liebreich, *Ber.*, 1870, **3**, 161) crystallises in large plates containing $4H_2O$; in the anhydrous form, it melts and decomposes at 242°. The *hydriodide*, $C_5H_{12}O_2NI$, melts at 188—190°, and is readily soluble in water or in boiling alcohol. A *compound*, $(C_5H_{11}O_2N)_2,KI,2H_2O$, crystallises from alcohol in glistening prisms, and, when anhydrous, melts and decomposes at 228—229°.

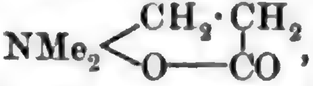
Ethyl dimethylaminoacetate boils at 149—150° (corr.), and is soluble in cold water, the *ethiodide* crystallises in short prisms melting at 71·5—72·5°.

Methyl diethylaminoacetate boils at 163·5° (corr.), is miscible with cold water in all proportions, but is only sparingly soluble in warm water; it yields a crystalline *aurichloride*, and a *methiodide* melting at 90—92°.

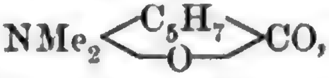
Dimethylaminodimethylacetal, $NMe_2{\cdot}CH_2{\cdot}CH(OMe)_2$, is a colourless, mobile liquid boiling at 137·5° (corr.), is miscible with water in all proportions, and has no reducing properties (Störmer and Prall, Abstr., 1897, i, 457).

Dimethylethylbetaine,  $NMe_2Et{<}\substack{CH_2\\O}{>}CO$, obtained by the action of silver oxide on the ethiodide of ethyl dimethylaminoacetate, crystallises from alcohol in four-sided plates melting and decomposing at 229—231°. The *platinichloride* is readily soluble, and the *aurichloride* crystallises in prisms decomposing at 236—237°. When the betaine is heated at 240—245°, it is transformed into *methyl methylethylaminoacetate* boiling at 151—152° (corr.). *Copper methylethylaminoacetate*, $C_{10}H_{20}O_4N_2Cu,3H_2O$, crystallises in deep blue, four-sided plates.

Methyldiethylbetaine crystallises in prisms containing $1H_2O$; in the anhydrous form, it melts at 133—135°.

Methyl β-dimethylaminopropionate, $NMe_2\cdot CH_2\cdot CH_2\cdot CO_2Me$, distils at 154·5°, forms a sparingly soluble *picrate*, a crystalline *aurichloride*, and a *methiodide* crystallising in plates or prisms and melting and decomposing at 191—192°. When warmed with alkalis, the methiodide yields acrylic acid and trimethylamine; with silver oxide, it gives *β-trimethylpropiobetaine*,  $NMe_2{<}\substack{CH_2\cdot CH_2\\O\text{——}CO}$, in the form of glistening needles containing $1H_2O$; when quickly heated, it melts and decomposes at 126°, but when slowly heated decomposes gradually at about 100°, the products formed being trimethylamine and acrylic acid. The *hydrochloride* crystallises in four-sided plates melting at 195—196°, the *aurichloride* crystallises in golden-yellow prisms melting and decomposing at 197—198°, and only sparingly soluble in water.

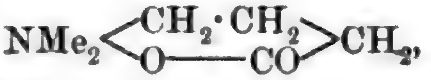
Dimethyltetrahydronicotinobetaine (*arecaidinmethylbetaine*),



$$NMe_2{<}\substack{C_5H_7\\O}{>}CO,$$

obtained from arecoline methiodide (Willstätter, Abstr., 1897, i, 385), crystallises in colourless, compact prisms containing $2H_2O$ and, when anhydrous melts and decomposes at 248°. The *platinichloride* and *aurichloride* both crystallise in plates. When the betaine is heated at 240°, it yields a base $C_7H_{13}N$, the *platinichloride* of which crystallises in pale red prisms melting at 116—118°, and the *aurichloride* in bronzy-yellow plates melting at 66—67°.

Methyl γ-dimethylaminobutyrate, $NMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2Me$, is a colourless oil distilling at 171·5—173° (corr.), and yields a crystalline *picrate* and *aurichloride*.

γ-Trimethylbutyrobetaine,  $NMe_2{<}\substack{CH_2\cdot CH_2\\O\text{——}CO}{>}CH_2$, crystallises in colourless plates containing $3H_2O$; in the anhydrous state, it begins to soften at 130° and decomposes at 222°. The *platinichloride* melts and decomposes at 224—225°, and the *aurichloride* crystallises in long, glistening needles. When heated, the betaine decomposes into trimethylamine and butyrolactone, as does also methyl γ-dimethylaminobutyrate at 205—225°.

J. J. S.

Serine and *iso*Serine. By Emil Fischer and Hermann Leuchs (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 78—87).—Serine, identical with that obtained from silk, is produced by allowing a mixture (in mol. proportions) of glycollic aldehyde and ammonia in alcoholic solution to stand for 24 hours, then adding the calculated quantity of hydrocyanic acid; after some time, an equal volume of hydrochloric acid is added, and 24 hours thereafter the cooled solution is saturated with hydrogen chloride. Ammonium chloride is removed by filtration, and the ammonia and chlorine by means of lead oxide; dissolved lead is removed from the filtrate by hydrogen sulphide and the filtrate evaporated in a vacuum, and then precipitated with alcohol. The crystals become brown at 225° and melt, with decomposition, at 246° (corr.). The solubility of the synthetical serine in water at 20° is 1 : 23·13.

Serine phenylcarbimide was prepared by the action of phenylcarbimide on serine in alkaline solution. It can be crystallised from hot water, melts at 168—169° (corr.), and is extremely easily soluble in alcohol.

When reduced with hydriodic acid, serine gives α-alanine. The synthesis and reduction indicate that serine is α-amino-β-hydroxypropionic acid.

iso*Serine* is obtained by heating β-chlorolactic acid with ammonia at 130°. *iso*Serine becomes brown at about 238° and melts, with decomposition, at 248° (corr.). The composition of the copper salt is $C_3H_5O_3NCu,3H_2O$, and it is probable that the alcoholic hydroxyl group plays a part in the formation of this.

iso*Serine phenylcarbimide* melts at 183—184° (corr.). It is easily soluble in alcohol, but almost insoluble in ether. When reduced with hydriodic acid, it gives β-alanine, so that *iso*serine is β-amino-α-hydroxypropionic acid.

Aldol-ammonia, when treated with hydrocyanic acid, gives *α-amino-γ-hydroxyvaleric acid*, which is soluble in hot water, has a sweet taste, and melts at 212°.

The authors purpose further to apply this method of Strecker's for the synthesis of α-amino-acids from hydroxyaldehydes. J. McC.

Action of Sulphuryl Chloride on Urethane. By FRITZ EPHRAIM (*Ber.*, 1902, **35**, 776—782).—A 25 per cent. yield of ethyl allophanate is obtained when urethane is treated with sulphuryl chloride in benzene solution. *Sulphourethane*, $SO_2[O\cdot C(OEt)\colon NH]_2$, obtained when the sodium derivative of urethane in benzene solution is treated with sulphuryl chloride, crystallises well from alcohol, melts at 171°, and forms crystalline *sodium* and *potassium* derivatives. When a boiling solution of urethane in benzene is treated with sodium, the *sodium* derivative of sodium allophanate, $NH_2\cdot C(ONa)\colon N\cdot CO_2Na$, is obtained; this forms star-shaped masses of crystals and is completely decomposed when treated with acids. Sulphuryl chloride seems to have no action on nitrourethane or aminosulphonic acid. R. H. P.

Action of Ammonia on Esters of Alkylmalonic Acids. By EMIL FISCHER and ALFRED DILTHEY (*Ber.*, 1902, **35**, 844—856).—The ethyl esters of malonic and of monoalkylated malonic acids react with both liquid and alcoholic ammonia, yielding the corresponding amides, and forming esters of malonamic acids as intermediate products. Esters of dialkylated malonic acids, on the other hand, yield either no amide or only minute traces. The compound described by Thorne (Trans., 1881, **39**, 545) as dimethylmalonamide is, in reality, monomethylmalonamide; it melts at 216·5° (corr.), and not at 207° as stated by Henry (*Jahresbericht*, 1889, 639). *Ethyl methylmalonamate*,

$$CO_2Et{\cdot}CHMe{\cdot}CO{\cdot}NH_2,$$

sublimes in colourless needles melting at 72·5°, and is readily soluble in water or alcohol.

Ethylmalonamide (Freund and Goldschmidt, Abstr., 1888, 675; Henry, *loc. cit.*) melts at 216° (corr.). *Ethyl ethylmalonamate* sublimes in colourless needles and melts at 77° (corr.). Propylmalonamide (Henry, *loc. cit.*) melts at 184° (corr.). *Ethyl propylmalonamate* crystallises in needles melting at 101° (corr.).

Ethyl dimethylmalonate yields only 2·6 per cent. of amide when heated at 145° for 30 hours with alcohol saturated with ammonia at 0°.

The amides of dialkylated malonic acids cannot be obtained from the corresponding ammonium salts, since when these are heated dialkylacetamides are produced. They may, however, be obtained by the action of ammonia on the acid chlorides (compare Franchimont, Abstr., 1886, 448).

Diethylmalonamide, $CEt_2(CO{\cdot}NH_2)_2$, crystallises from boiling water in prisms melting at 224° (corr.) and is practically insoluble in ether. *Dipropylmalonamide*, obtained from the chloride, which boils at 221—223°, crystallises in long needles and melts at 214° (corr.). *Dimethylmalonamide* melts at 261° (corr.).

Ethyl phenylacetate yields an amide much more readily than ethyl benzoate.

Ethyl trimethylacetate does not react with ammonia to yield an amide.

Malonamide, propylmalonamide, and diethylmalonamide have been hydrolysed with sodium hydroxide; the amounts decomposed after boiling for 42 minutes were respectively 89, 57, and 3 per cent. Dimethylmalonamide is much more readily hydrolysed than diethylmalonamide. J. J. S.

Production of the Imides of Succinic and Glutaric Acids by the Partial Hydrolysis of the Corresponding Nitriles.

By MARSTON T. BOGERT and DAVID C. ECCLES (*J. Amer. Chem. Soc.*, 1902, **24**, 20—25).—When succinonitrile (2 mols.) is heated in a sealed tube with water (4 mols.) and sulphuric acid (1 mol.), a brown, crystalline product is obtained, which consists of a mixture of β-cyanopropionic and succinic acids and their amides, succinamic acid, succinimide, ammonium sulphate, and unchanged succinonitrile. The best yield of succinimide is obtained by heating for about 2 days at 165—175°. If the nitrile (1 mol.) is heated with water (2 mols.) in the absence of sulphuric acid for 5 hours at 153—173°, very little imide is produced and most of the nitrile remains unaltered. When the nitrile (1 mol.) is heated with water (1 mol.) for 6 hours at 153—173°, a large quantity of succinimide is formed, together with a small amount of succinamic acid, traces of succinamide, but no cyanopropionamide.

If glutaronitrile (2 mols.) is heated in a sealed tube with water (4 mols.) and sulphuric acid (1 mol.) for 5—10 hours at 155—200°, glutarimide is obtained in a yield of 60 per cent., but no amide or amic acid can be detected. E. G.

Thiuram Disulphides and *iso*Thiuram Disulphides. I. By JULIUS VON BRAUN (*Ber.*, 1902, **35**, 817—830. Compare Abstr., 1900, i, 644).—It is shown that alkylammonium salts of alkylated dithiocarbamic acids on oxidation with iodine, bromine, hydrogen peroxide, or potassium persulphate, readily yield thiuram disulphides, for example, $R^1\cdot NH\cdot CS\cdot SH\cdot NH_2R^2 + I_2 = S_2(CS\cdot NHR^1)_2 + 2NH_2R^2,HI$.

Tetramethylthiuram disulphide, $S_2(CS\cdot NMe_2)_2$, prepared by oxidising an alcoholic solution of dimethylamine dimethylthiocarbamate, forms small, white crystals melting at 146°. *Tetrapropylthiuram disulphide*, $S_2(CS\cdot NPr^a{}_2)_2$, is obtained by oxidising the corresponding dithiocarbamate and melts at 50°.

Diphenyldimethylthiuram disulphide, $S_2(CS\cdot NMePh)_2$, prepared by adding iodine to an alcoholic solution of mol. proportions of methylaniline and carbon disulphide, melts at 198°. The corresponding *diethyl* compound is prepared by oxidising a mixture of ethylaniline and carbon disulphide with hydrogen peroxide; it melts at 169—170°.

Dimethyl- and diethyl-thiuram disulphides (m. p. 102° and 75°) can similarly be obtained from an alcoholic solution of the base and carbon disulphide; the following hitherto undescribed dialkylthiuram disulphides have also been prepared; *dipropylthiuram disulphide*, $S_2(CS\cdot NHPr^a{}_2)_2$, melting at 58°; *diisopropylthiuram disulphide*, melting at 69°; *diisobutylthiuram disulphide*, melting at 51°; *diisoamylthiuram disulphide*, melting at 61—62°; *dibenzylthiuram disulphide*, melting at 71°. These dialkylthiuram disulphides readily decompose into the corresponding thiocarbimides, hydrogen sulphide, and sulphur on the one hand, or, on the other hand, into thiocarbamides, carbon disulphide, and sulphur. With the more simple alkyl groups, the first decomposition is more prominent; with the more complex alkyl groups, the second decomposition mainly occurs.

The neutral dialkylthiuram disulphides are converted by alcoholic potash into isomeric *iso*thiuram compounds, which are acid in character, and form a series of metallic salts.

S-*Dimethylisothiuram disulphide*, $S_2[C(SMe):NH]_2$, is obtained when methyl iodide acts on thiuram disulphide dissolved in alcohol containing sodium ethoxide; it is also formed by the action of alcoholic sodium hydroxide on the isomeric dimethylthiuram disulphide; it crystallises in colourless needles from benzene, melting at 85°. With concentrated acids, methyl mercaptan is formed.

N-*Dimethyl*-S-*dimethylisothiuram disulphide*, $S_2[C(SMe):NMe]_2$, prepared from dimethylthiuram disulphide, is a liquid boiling at 100° under 12 mm. pressure. N-*Dibenzyl*-S-*dipropylisothiuram disulphide*, $S[C(SPr_a):N\cdot CH_2Ph]_2$, prepared from dibenzylthiuram disulphide and propyl bromide, is a pale red liquid, boiling at 175° under 12 mm. pressure.

With iodine, the salts of *iso*thiuram disulphides yield quantitatively sulphur and alkylthiocarbimides.

The mechanism of the reactions by which the substances described in this paper are produced, are fully discussed. K. J. P. O.

Ferric Ferrocyanide. By J. MATUSCHEK (*Chem. Zeit.*, 1902, **26**, 41—43. Compare Abstr., 1901, i, 262, 454, 635, 677).—By the action of oxalic acid on potassium ferrocyanide, with access of oxygen, blue precipitates are obtained which have the composition of Prussian blue but exhibit a coppery lustre, and are therefore to be designated as Paris blue. The blue precipitate is not produced in the dark, and temperature, as well as the concentration of the solutions, has an influence on the formation of the precipitate. A. F.

Double Cyanides of Thallium. By TH. FISCHER and R. BENZIAN (*Chem. Zeit.*, 1902, **26**, 49—50).—*Thallium ferrocyanide.* On adding a hot concentrated solution of thallous sulphate to potassium ferrocyanide and allowing the mixture to cool, the yellow, crystalline double salt, $Tl_4Fe(CN)_6,2H_2O$ is obtained. It is sparingly soluble in cold, more readily in hot, water (compare Crookes, *Chem. News*, 1861, **3**, 303). From the aqueous solution, hydrochloric acid precipitates thallous chloride; potassium iodide, thallous iodide; baryta water, barium ferrocyanide; and silver nitrate, silver ferrocyanide. Alkalis and dilute nitric and sulphuric acids have no action on the aqueous solution of the thallium ferrocyanide, but concentrated acids decompose it. By mixing dilute solutions of potassium ferrocyanide and thallous sulphate, precipitating with alcohol and recrystallising the precipitate from water, yellow plates are obtained of the composition

$$K_4Fe(CN)_6,K_3TlFe(CN)_6,6H_2O.$$

This salt is isomorphous with potassium ferrocyanide, and behaves towards reagents like thallium ferrocyanide, but is more soluble in cold water.

Thallium ferricyanide. On adding thallous sulphate to a solution of potassium ferricyanide, a dark red solution is obtained from which, on concentration in a vacuum, red needles having the composition $K_2TlFe(CN)_6$ separate. This salt is decomposed by pure water, but the decomposition is prevented by the presence of potassium ferricyanide, and from the solution containing the latter salt red prisms of the composition $4K_3Fe(CN)_6,3K_2TlFe(CN)_6$ are deposited on evaporation. Double salts of the composition $Tl_5KFe_2(CN)_{12}$, and mixtures of $K_2Tl_4Fe_2(CN)_{12}$ and $K_3Tl_3Fe_2(CN)_{12}$, are obtained by employing thallium phosphate instead of thallous sulphate. *Thallium chromicyanide* is obtained in bright yellow, anhydrous plates by heating thallous sulphate with excess of basic lead chromicyanide and concentrating the solution in a vacuum over sulphuric acid. It has the composition $Tl_3Cr(CN)_6$. On shaking a warm concentrated solution of potassium chromicyanide with thallous cyanide and concentrating the resulting solution in a vacuum, bright yellow crystals of the composition $K_2TlCr(CN)_6$ are obtained which are isomorphous with those of potassium chromicyanide. Both these chromicyanogen compounds are soluble in water. *Thallium cobalticyanide* is obtained by neutralising an aqueous solution of hydrocobalticyanic acid with thallous hydroxide and concentrating the solution in a vacuum. It has the composition $Tl_3Co(CN)_6$, and shows all the properties of the salt as described by Fronsmüller (Abstr., 1878, 395). The salt is fairly readily soluble in hot 50 per cent. alcohol, and crystallises out almost completely on cooling. A potassium thallium salt of the composition $K_3Tl_3Co(CN)_{12}$ is obtained by mixing hot concentrated solutions of potassium cobalticyanide and dibasic thallous phosphate. It is much more readily soluble in cold water than thallium cobalticyanide. A. F.

Dichloro-acetyl Phosphide. By P. N. EVANS and C. E. VANDERKLEED (*Amer. Chem. J.*, 1902, **27**, 142—146).—Dry hydrogen phosphide was passed into dichloro-acetyl chloride for some hours. After some time, a large quantity of ether was added and a gummy mass was precipitated which gradually solidified to a faintly yellow powder. Analysis showed that the powder has the formula $CHCl_2{\cdot}CO{\cdot}PH_2$. It chars without melting at 200° and is insoluble in ether, benzene, or chloroform, but very easily soluble in alcohol. It is slowly decomposed by water with evolution of hydrogen phosphide. J. McC.

Composition of Norwegian Wood Tar. By J. ALFRED MJÖEN (*Zeit. angew. Chem.*, 1902, **15**, 97—111).—Various wood tars have been investigated, namely: I, Norwegian retort tar, obtained by distillation of pinewood sawdust; II, a tar obtained by peasants in Gudbransdale; III, Austrian beech-wood tar; IV, Bohemian pinewood tar. The tar was in each case treated as far as possible under conditions not favourable to chemical change, for example, all distillations were carried on under reduced pressure, and as far as possible in absence of air, and the various fractions obtained were kept in the dark.

	I.	II.	III.	IV.	
Aqueous solution	4·45	5	7·2 strongly acid	3·7	per cent.
Acetone	0·4	0·07	—	—	„
Total aldehydes and ketones	0·8	0·5	—	—	„
Acetic acid	0·36	0·37	—	—	„
Total fatty acids	3·64	1·78	Acetic, propionic, butryic, and valeric were detected.		
Guaiacol and creosote	creosote 20·0		guaiacol 10·5	cresote 7·5	per cent.
Phenols and phenolic derivatives	44·7	21·5	41·0	17·0	„
Retene	none	4—5	—	—	„
Pitch	20·6	10·1	21·0	29·0	„
Hydrocarbons and neutral substances	22·5	*46·0	18·0	40·0	„
Esters	—	1·4	—	—	„
Alcohols	1·0	—	—	—	„

* About 20 per cent. aliphatic and 80 per cent. aromatic hydrocarbons.

Nitrogen and sulphur compounds were not present, but certain unsaturated compounds were isolated.

The retort tar has a characteristic unpleasant odour quite different from that of the Finnish tar largely used in Norway, and also differs from the latter in the relatively large amounts of soluble fatty acids present. J. J. S.

Stereochemistry of Benzene. By WILHELM MARCKWALD (*Ber.*, 1902, **35**, 703).—In reference to Graebe's discussion on the space formula of benzene (compare this vol., i, 209) the author states that all those configurations which do not contain the centres of gravities of their constituent atoms in the same plane may be *a priori* excluded on purely stereochemical grounds. G. T. M.

Action of Bromine on Durene and Penta- and Hexa-methylbenzenes. By ANTON VON KORCZYNSKI (*Ber.*, 1902, **35**, 868—872).—The influence of sunlight in facilitating the entry of bromine into the side chain is not observable in the case of the higher methylbenzenes. Hexamethylbenzene is not attacked by bromine in sunlight, whilst pentamethylbenzene and durene yield substitution derivatives; in the dark, durene yields a mixture of mono- and dibromo-durene and in sunlight monobromodurene only.

On passing bromine vapour into durene at 100°, substitution in the side chain occurs; a small quantity (about 7 per cent.) of a *durylene dibromide*, $C_6H_2Me_2(CH_2Br)_2$, crystallising from alcohol in white needles and melting at 157° was isolated. It was converted by alcoholic potassium acetate into *durylene diacetate*, $C_6H_2Me_2(CH_2{\cdot}OAc)_2$, which crystallises from alcohol in thin, iridescent leaflets and melts at 65°; *durylene glycol*, $C_6H_2Me_2(CH_2{\cdot}OH)_2$, forms thin, white scales, melts at 74°, and on oxidation with aqueous potassium permanganate yields a *xylenedicarboxylic acid* crystallising from alcohol in leaflets and melting at 123° W. A. D.

***p*-Nitrobenzenesulphonic Acid.** By ALFRED EKBOM (*Ber.*, 1902, **35**, 651—656. Compare Blanksma, Abstr., 1901, 461).—Limpricht's statements (this Journal, 1875, 1027) with regard to *p*-nitrobenzenesulphonic acid are incorrect; its chloride is not a liquid, but separates from light petroleum in monoclinic crystals [$a:b:c = 1{\cdot}3042:1:1{\cdot}1369$; $\beta = 74°21'$] melting at 79·5—80·5°, whilst the amide forms monoclinic prisms [$a:b:c = 0{\cdot}6501:1:0{\cdot}5184$; $\beta = 79°48'$] and melts at 177—178°, not at 131°.

On heating the sulphonic chloride with hydriodic acid of sp. gr. 1·5, it is converted into Willgerodt's *p*-dinitrodiphenyl disulphide (Abstr., 1885, 519), which melts at 180—181°, not at 168—170° as stated by Leuckart (Abstr., 1890, 604); the structure of the acid is thus established. Potassium *p*-nitrobenzenesulphonate, obtained from the pure sulphonic chloride, crystallises in prismatic scales with $1H_2O$, and is not anhydrous as stated by Limpricht. W. A. D.

***p*-Halogen-arylthiosulphonates.** By JULIUS TROEGER and F. HURDELBRINK (*J. pr. Chem.*, 1902, [ii], **65**, 82—90).—When iodobenzene is heated with fuming sulphuric acid and the product treated with solution of sodium chloride, sodium *p*-iodobenzenesulphonate is produced together with some 1 : 4-di-iodobenzene. By the action of phosphorus pentachloride on sodium *p*-iodobenzenesulphonate, *p*-iodobenzenesulphonic chloride is obtained, and is converted by potassium sulphide into *potassium* p-*iodothiobenzenesulphonate*. This salt was not obtained pure, but was converted into the *aniline* salt, which forms a white, amorphous precipitate and melts at 138°. The *benzidine* salt, $C_6H_4I\cdot S\cdot SO_2H,C_{12}H_8(NH_2)_2$, forms small crystals, and melts and decomposes at 204—206°.

p-*Iodobenzenesulphinic acid*, $C_6H_4I\cdot SO_2H$, obtained by the action of hydrochloric acid on potassium *p*-iodothiobenzenesulphonate, melts at 137° and dissolves readily in ether or alcohol and sparingly in water; its *sodium* salt crystallises with $4H_2O$. By the action of iodine on this sodium salt, p-*iodobenzenesulphonic iodide*, $C_6H_4I\cdot SO_2I$, is produced, which crystallises in small, golden-yellow leaflets and melts at 95°; it is converted by ammonia into *p*-iodobenzenesulphonamide. When *p*-iodobenzenesulphinic acid is heated with water in a sealed tube for 8 hours at 130°, p-*iodobenzene disulphoxide*, $(C_6H_4I\cdot SO)_2$, is obtained, which crystallises in white leaflets, melts at 193°, and is readily soluble in alcohol or ether.

The *potassium* salt of p-*bromobenzenethiosulphonic acid*, prepared from *p*-bromobenzenesulphonic chloride and potassium sulphide, was not obtained pure, but was converted into the p-*phenylenediamine* salt, $(C_6H_4Br\cdot SO_2\cdot SH)_2,C_6H_4(NH_2)_2$, which melts and decomposes at 155°; the *aniline* salt was also prepared.

Sodium p-*chlorobenzenethiosulphonate*, $C_6H_4Cl\cdot SO_2\cdot SNa,2H_2O$, was obtained by the action of sodium sulphide on *p*-chlorobenzenesulphonic chloride; the p-*phenylenediamine* salt crystallises in needles; the *benzidine* salt was also prepared. E. G.

Thiocarbimides and Thiocarbamides derived from Terpenes.

By JULIUS VON BRAUN and K. RUMPF (*Ber.*, 1902, **35**, 830—833).—Methyl*cyclo*hexylamine, camphylamine, pinylamine, thujylamine, and *l*-menthylamine readily combine with carbon disulphide, yielding dithiocarbamates, which on oxidation (Abstr., 1900, i, 644) yield liquid disulphides. When heated, these disulphides are decomposed into sulphur, carbon disulphide, and dialkylthiocarbamides, or, when treated with iodine, they yield the corresponding thiocarbimides which combine with the original bases forming dialkylthiocarbamides.

*Methyl*cyclo*hexylthiocarbimide*, $C_7H_{13}\cdot N:CS$, boils at 115·5° under 13 mm. pressure and reacts with aniline, yielding phenylmethyl*cyclo*hexylthiocarbamide melting at 92°. *Dimethyl*cyclo*hexylthiocarbamide* melts at 119°. Camphylthiocarbimide (Goldschmidt and Schulhof, Abstr., 1886, 557) boils at 160° under 25 mm. pressure. *Dicamphylthiocarbamide* is an oil. *Pinylthiocarbimide* boils at 142—143° under 14 mm. pressure, and *dipinylthiocarbamide* melts at 189°. *Thujylthiocarbimide* boils at 126—128° under 14 mm. pressure. *Thujylphenylthiocarbamide* melts at 107—108°. *Menthylthiocarbimide* distils at 138° under 12 mm. pressure, and *dimenthylthiocarbamide* melts at 200°.

J. J. S.

Oxidation of Methyl- and Ethyl-aniline.

By EUGEN BAMBERGER and MICHAEL VUK (*Ber.*, 1902, **35**, 703—714. Compare Abstr., 1900, i, 435; 1901, i, 200, 587).—When oxidised with hydrogen peroxide, methylaniline yields a mixture of nitrobenzene, azobenzene, and azoxybenzene; this oxidation proceeds so slowly that the intermediate products undergo further changes before the reaction is complete, and the substances isolated represent only the final stage of the process. The use of Caro's reagent, persulphuric acid, brings about a more rapid oxidation and permits of the isolation of the intermediate products. The secondary base is suspended in water or in ether and treated with a neutralised solution of Caro's reagent at 0—8°; formaldehyde, nitrosobenzene, nitrobenzene, azobenzene, azoxybenzene, β-phenylhydroxylamine, β-methylenebis-β-phenylhydroxylamine, $CH_2(NPh\cdot OH)_2$, and diphenylhydroxyformamidine, $NPh\colon CH\cdot NPh\cdot OH$, have been identified with certainty, whilst the product also contains a substance having the properties of β-formylphenylhydroxylamine, $CHO\cdot NPh\cdot OH$. In all probability, the methylaniline is first oxidised to β-phenylmethylhydroxylamine, $NMePh\cdot OH$, which, however, is not isolated, but undergoes further oxidation either into β-formyl-β-phenylhydroxylamine or β-phenylhydroxylamine. In the second stage of the oxidation, formaldehyde is liberated, and a portion of this compound reacts with β-phenylhydroxylamine yielding β-methylenebis-β-phenylhydroxylamine; the methylene compound subsequently loses water, giving rise to diphenylhydroxyformamidine. Nitrobenzene, nitrosobenzene, and azoxybenzene result from the further oxidation of β-phenylhydroxylamine, whilst this hydroxylamine derivative probably condenses with methylaniline to furnish azobenzene; the methyl alcohol, which should result from this interaction, has, however, not been isolated.

Ethylaniline, when oxidised with hydrogen peroxide, yields azobenzene, azoxybenzene, and nitrobenzene, together with a small quantity of a substance having the characters of an aminophenol. With Caro's reagent, the secondary amine gives rise to nitrobenzene, nitrosobenzene, azobenzene, and azoxybenzene.

A small amount of an acidic substance, which corresponds in properties with β-acetyl-β-phenylhydroxylamine, is simultaneously produced.

Methylaniline and nitrosobenzene, when condensed in cold glacial acetic acid, yield a mixture of aniline, azobenzene, and azoxybenzene.

G. T. M.

Oxidation of Methylenebisaniline. By EUGEN BAMBERGER and FRED. TSCHIRNER (*Ber.*, 1902, **35**, 714—730. Compare preceding abstract).—The oxidation of methylenebisaniline, $CH_2(NHPh)_2$, with Caro's acid shows that the reaction involves a partial hydrolysis of the diamine into aniline and formaldehyde, each of these substances having been isolated in the final product; the former, however, is partially oxidised to azoxybenzene, nitrobenzene, and nitrosobenzene, and the latter to formic acid and carbon dioxide.

Anhydro-*p*-hydroxylaminobenzyl alcohol is also a product of this reaction and results from the simultaneous oxidation and hydrolysis of the methylene base.

Oxidation of the methylene base without hydrolysis leads to the production of diphenylformamidine, $NPh\colon CH\cdot NHPh$, and diphenyl *N*-hydroxyformamidine, $NPh\colon CH\cdot NPh\cdot OH$; the latter of these amines, by hydrolysis and intramolecular transformation, gives rise to *p*-nitrophenol, a trace of the ortho-isomeride being simultaneously produced. Substances having properties resembling those of *p*-aminobenzaldehyde and β-formyl-β-phenylhydroxylamine are found amongst the products of oxidation, but the compounds themselves have not been isolated.

Diphenylhydroxyformamidine is first isolated in the form of its hydrate, NPh:CH·NPh·OH,H_2O, melting indefinitely at 94—95°; the anhydrous base is obtained by drying the hydrate over concentrated sulphuric acid in a vacuum. The *hydrochloride*, *nitrate*, and *copper* compound, $Cu(O·NPh·CH:NPh)_2$, are derivatives of the anhydrous base; the acid salts crystallise in silky needles and the metallic derivative separates from its solution in the ordinary organic solvents in light red, felted needles melting at 240—241°. G. T. M.

Oxidation of Benzylaniline. By Rudolf Hübner (*Ber.*, 1902, **35**, 731. Compare preceding abstracts).—Benzylaniline, when treated with Caro's reagent in neutral solutions, yields nitrosobenzene, nitrobenzene, azoxybenzene, and benzoic acid. G. T. M.

Isomerism of Quaternary Ammonium Bases. By Arthur Hantzsch and Arthur Horn (*Ber.*, 1902, **35**, 883—888).—Wedekind's isomeric α- and β-salts of phenylbenzylmethylallylammonium (Abstr., 1899, i, 351; 1900, i, 155) were examined in order to ascertain whether they differed structurally, and especially whether one of them might contain an *iso*allyl or propyl, in place of an allyl, group; both substances were found, however, to be unsaturated towards bromine and permanganate, and to yield formic, and not acetic, acid on oxidation with 33 per cent. nitric acid. T. M. L.

Simple and Double Dissociation of Quaternary Ammonium Salts. By Edgar Wedekind [and, in part, F. Oberheide] (*Ber.*, 1902, **35**, 766—776. Compare Abstr., 1900, i, 155, and Pope and Harvey, Trans., 1901, **79**, 831).—Ethyl phenyldimethylammoniumiodoacetate (Abstr., 1901, i, 640) crystallises in the rhombic system [$a:b:c = 0·9222:1:0·6912$]; the corresponding *methyl* ester separates from alcohol in small, yellow, triclinic crystals, which melt at 104—105°; either ester, when heated in an oil-bath at 130° for three-quarters of an hour, yields phenyltrimethylammonium iodide. *Methyl* p-*tolyldimethylammoniumiodoacetate*, prepared from dimethyl-*p*-toluidine and methyl iodoacetate, separates from water in monoclinic crystals [$a:b:c = 1·8080:1:1·1878$, $\beta = 84°43'$], which soften at 120°, melt and decompose at 124—125°, and, when heated, yield p-*tolyltrimethylammonium iodide*; this crystallises from alcohol and volatilises at 216—220°. Ethyl methyltetrahydroquinoliniumiodoacetate, when heated at 120°, yields *dimethyltetrahydroquinolinium iodide*, which crystallises in small, colourless prisms melting at 176°; by silver oxide, the iodide is converted into the *base*, which forms a *platinichloride*, $C_{22}H_{32}N_2PtCl_6$, crystallising in lustrous tablets and melting at 216°. *Methyl tripropylammoniumiodoacetate* crystallises in lustrous, rhombic leaflets or in large, yellowish prisms [$a:b:c = 0·9041:1:0·6975$], which melt at 173—174° and decompose at about 200°; *tripropylammonium iodide* decomposes at about 280° and can be crystallised from dilute alkalis; *methyltripropylammonium iodide* crystallises in lustrous leaflets and melts at 207—208°.

Methyl pyridiniumiodoacetate, prepared from pyridine and methyl iodoacetate, separates from water in colourless crystals, which decompose at 144—145°, and forms an iodine additive *compound*, $C_8H_{10}O_2NI,I_2$, which crystallises from alcohol and decomposes at 102—104°.

Phenacylphenyldimethylammonium bromide is deliquescent, crystallises from alcohol or ether, sinters at about 115°, and melts at 125—128°. *Phenacyl*-p-*tolylmethylethylammonium bromide* crystallises in colourless needles and melts at 116—117° without decomposition.

R. H. P.

Aromatic Polycarbylamines. By FELIX KAUFLER (*Monatsh.*, 1901, **22**, 1073—1082).—Previous failures to obtain polycarbylamines have been due to the instability of these substances in boiling alcoholic potash. By using an excess of chloroform and a concentrated aqueous solution of potassium hydroxide containing 20—40 per cent. of alcohol, the author has obtained dicarbylamines from *p*- and *m*-phenylenediamine. p-*Phenylenedicarbylamine* forms white, triclinic needles and plates [$a:b:c = 0.8489:0.9571:1$; $\alpha = 87°42'$; $\beta = 105°15'$; $\gamma = 107°38'$] which darken on exposure to air and commence to blacken at 140°. A mol. weight determination showed that polymerisation had not taken place. With bromine dissolved in ether, the dicarbylamine forms p-*phenylenedicarbylamine tetrabromide*, which crystallises from ether in long, glistening, colourless needles melting at 137—138°. On exposure to light, the crystals become violet, the change of colour being accompanied by loss of bromine. On boiling the compound with absolute methyl alcohol, the bromine is entirely eliminated, and the tetrabromide also reacts with boiling aniline. Isomeric change of the dicarbylamine into terephthalonitrile commences at 160°, and takes place with explosive violence between 230° and 260°. The nitrile melts at 222—223° (corr.), and is hydrolysed by dilute hydrochloric acid to terephthalic acid. The dicarbylamine reacts energetically with acetyl chloride and with benzoyl chloride, is decomposed by boiling dilute acids and alkalis, and is instantly charred by concentrated sulphuric acid. It decolorises potassium permanganate in acid and alkaline solutions.

m-*Phenylenedicarbylamine* forms long, light yellow needles, which, when exposed to air, change into a dark brown, amorphous mass. The crystals blacken at 80° and melt at 95° with evolution of gas. The dicarbylamine decolorises potassium permanganate and bromine solutions. When heated, it is converted into *iso*phthalonitrile melting at 154—155°, which on hydrolysis gives *iso*phthalic acid melting at 310—320°.

The action of chloroform and potassium hydroxide on 2 : 4-diamino-1 : 3 : 5-trimethylbenzene yields needles which cannot be purified, but which, on heating, change into 2 : 4-dicyano-1 : 3 : 5-trimethylbenzene. With 2 : 4 : 6-triaminotoluene, the reaction gives a small quantity of a substance having the characteristic odour of the carbylamines. Triaminomesitylene yields a substance which blackens at 160°, and has the odour of a carbylamine. The analytical results agree with those required by 4 : 6-*diisocyano*-2-*hydroxy*-1 : 3 : 5-*trimethylbenzene*.

G. Y.

Action of Alcoholic Potassium Hydroxide or Formaldehyde on Nitrosobenzene. By EUGEN BAMBERGER (*Ber.*, 1902, **35**, 732—738).—N-*Formyl-β-phenylhydroxylamine* results from the action of potassium hydroxide dissolved in ethyl alcohol on nitrosobenzene; it crystallises from hot water or any of the ordinary mineral solvents in colourless plates or silky needles and melts at 70—71°. In aqueous ferric chloride solution, the formyl compound develops an intense reddish-violet coloration, which changes to greenish-brown on the addition of strong hydrochloric acid. The *copper* derivative, $Cu(O{\cdot}NPh{\cdot}CHO)_2$, is insoluble in water, but crystallises from alcohol in light green, flattened needles; its decomposition point is ill-defined, lying between 225° and 230°.

When the nitrosobenzene and potassium hydroxide are dissolved in methyl alcohol, the reaction leads to the formation of azoxybenzene, nitrobenzene, and *p*-aminophenol; *N*-formyl-*β*-phenylhydroxylamine is not produced.

Formaldehyde and nitrosobenzene react in methyl alcohol solution, giving rise to azoxybenzene, *N*-formyl-*β*-phenylhydroxylamine, aniline, and probably traces of formanilide and *p*-aminophenol. G. T. M.

α-Naphthylamine Derivatives. By V. FUSSGANGER (*Ber.*, 1902, **35**, 976—984. Compare Friedländer and Welmans, Abstr., 1889, 150).—When dimethyl-α-naphthylamine is heated with 90 per cent. sulphuric acid at 130°, a mixture of two monosulphonic acids is obtained, which may be separated by the aid of cold water, in which the 5-sulphonic acid is practically insoluble. The positions of the sulphonic acid groups were established by alkylating the various 1-naphthylaminesulphonic acids and comparing these products with the two acids obtained by sulphonating the alkylated base.

1-*Dimethylaminonaphthalene-4-sulphonic acid*, $NMe_2{\cdot}C_{10}H_6{\cdot}SO_3H$, obtained by the action of methyl iodide, methyl alcohol, and sodium hydroxide (1 mol.) on naphthionic acid at 100—110° for 6—8 hours, crystallises from hot water in well-developed, quadratic prisms containing $1H_2O$. With concentrated hydrochloric acid, it forms a soluble salt which is hydrolysed by water.

The *dimethylamino-5-sulphonic acid* also crystallises with $1H_2O$ in quadratic prisms and closely resembles the 4-acid. Its solutions exhibit a green fluorescence, and when fused with potash, it yields 1-*dimethylamino-5-hydroxynaphthalene* in the form of hexagonal plates melting at 110° and identical with the compound described in the D.R.-P. No. 50142. With *p*-nitrosodimethylaniline, it yields a greenish-blue *dye*, probably *tetramethyldiaminonaphthaphenoxazonium chloride*,

$$NMe_2{\cdot}C_{10}H_5{<}{\overset{N}{\underset{O}{}}}{>}C_6H_3{:}NMe_2Cl\,;$$

it dissolves readily in water and is a strong base, is turned violet by concentrated sulphuric acid, and gives a pure indigo blue on cotton mordanted with tannic acid or tartar emetic. The similar *dye* obtained from nitrosodiethylaniline is somewhat greener in colour.

5-Dimethylamino-α-naphthol and *p*-nitroso-*m*-dimethylaminophenol yield a pure blue dye, which is turned yellowish-red by concentrated sulphuric acid. Nitrous acid reacts with 5-dimethylamino-α-naphthol suspended in acetic acid, yielding 6-*nitroso*-1-*dimethylamino*-5-*hydroxynaphthalene* (1-*dimethylamino*-5 : 6-*naphthaquinoneoxime*) in the form of yellow, pointed needles, and condenses with amines and aminophenols to form quinoneimide dyes.

1-*Diethylaminonaphthalene*-5-*sulphonic acid* crystallises with $1H_2O$ in long, colourless needles and dissolves in concentrated hydrochloric acid, dilute alkalis, or alcohol.

1-*Methylaminonaphthalene*-6-*sulphonic acid*, obtained by methylating α-naphthylamine-6-sulphonic acid, forms a soluble *sodium* salt which crystallises with $1H_2O$.

1-*Dimethylaminonaphthalene*-7-*sulphonic acid* is readily soluble in water, and its *sodium* salt crystallises in colourless plates containing $1H_2O$.

1-*Dimethylaminonaphthalene*-8-*sulphonic acid* forms a soluble sodium salt containing $1H_2O$, and the free acid is readily soluble in both dilute acids or alkalis. J. J. S.

Naphthalenoid Carbamide and Thiocarbamide Sulphonic Acids containing free Hydroxyl Groups. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 123693).—When a mixture of 6-amino-α-naphthol-3-sulphonic acid and 7-amino-α-naphthol-3-sulphonic acid, dissolved in an aqueous solution of sodium carbonate, is treated with carbonyl chloride, *carbonyl*-8 : 5′-*dihydroxydi*-β-*naphthylamine*-6 : 7′-*disulphonic acid*, $CO[NH\cdot C_{10}H_5(OH)\cdot SO_3H]_2$, is obtained as a soluble, grey powder which combines with diazonium salts but is not affected by nitrous acid. The corresponding *thiocarbonyl* compound,

$$CS[NH\cdot C_{10}H_5(OH)\cdot SO_3H]_2,$$

produced by substituting thiocarbonyl chloride for its oxygen analogue in the preceding reaction, is a soluble, white powder. Carbonyl derivatives of other aminonaphtholsulphonic acids are also described (compare D.R.-P. 116200). G. T. M.

Preparation of Iodine Substitution Derivatives of Phenols. By E. RICHARD (*J. Pharm. Chim.*, 1902, [vi], **15**, 217—221).—Iodine substitution derivatives of phenols are readily prepared by the action of an aqueous solution of iodine on an aqueous solution of the phenol, containing either sodium hydrogen carbonate, disodium hydrogen phosphate, or sodium acetate. The hydriodic acid liberated by the action of the iodine on the phenol reacts with the added sodium salt with formation of sodium iodide. Sodium hydrogen carbonate can only be used in those cases in which substitution takes place without the application of heat. Several mono-, di-, and tri-iodophenols have been prepared by this method. H. R. LE S.

Iodophenols. By P. BRENANS (*Compt. rend.*, 1902, **134**, 357—360).—The tri-iodophenol obtained by the action of iodine on sodium phenoxide (Abstr., 1883, 1109) is the 2 : 4 : 6-derivative, and the di-iodophenol formed in the same way is the 2 : 6-derivative. The latter yields 3 : 5-di-iodo-*p*-hydroxybenzaldehyde when treated with chloroform and potassium hydroxide, and the 2 : 4 : 6-tri-iodide when treated with iodine and mercuric oxide. The tri-iodophenyl allyl ether, prepared from this tri-iodophenol, melts at 156°. Derivatives of the di-iodophenol were prepared as follows: *di-iodoanisole*, in prismatic crystals melting at 35°; *di-iodophenetole*, in prismatic crystals melting at 41—42; *di-iodophenyl allyl ether*, in tabular crystals melting at 46°; *di-iodophenyl benzyl ether*, in prisms melting at 74·5°. When treated with fuming nitric acid, the di-iodophenol yields 4-nitro-2 : 6-iodophenol melting at 156·5°, and this yields a *methyl ether* in acicular crystals melting at 133—134°, and an *acetate* in similar crystals melting at 194—195°. The action of the nitric acid also yields a 6-nitro-2-iodophenol melting at 110°; its *methyl ether* melts at 60—61°, and its *acetate* at 96—97°.

The action of nitric acid on *o*-iodophenol yields 2-iodo-6-nitrophenol melting at 110°, and 2-iodo-4-nitrophenol melting at 86—87°. The latter yields a *methyl ether* melting at 97°, and an *acetate* melting at 68° (compare Busch, *Ber.*, 1874, **7**, 462). C. H. B.

2-Cyano-4 : 6-dinitrophenol and some of its Derivatives. By J. J. Blanksma (*Rec. Trav. Chim.*, 1901, **20**, 411—421).—*o*-Ethoxybenzonitrile on nitration yields 3 : 5-*dinitro-2-ethoxybenzonitrile*, which crystallises in leaflets melting at 72°. Its properties are in every way similar to those of the ethyl ether of picric acid. With ammonia, the ethoxy-group is replaced by an amino-group, 2-*amino*-3 : 5-*dinitrobenzonitrile*, $CN\cdot C_6H_2(NO_2)_2\cdot NH_2$, being produced; it forms yellow crystals melting at 219°, and does not react with carbon disulphide or benzaldehyde. With phenylhydrazine, 2-*cyano*-4 : 6-*dinitrohydrazobenzene*,

$$CN\cdot C_6H_2(NO_2)_2\cdot N_2H_2Ph,$$

is obtained as red crystals decomposing at 270—280°; with hydrazine, 2-*cyano*-4 : 6-*dinitrophenylhydrazine* is formed as red crystals decomposing at 280°, and with hydroxylamine, 2-*cyano*-4 : 6-*dinitrophenylhydroxylamine*, which forms yellow crystals melting at 200°. With alkali hydroxides, the ethyl ether is converted into 2-*cyano*-4 : 6-*dinitrophenol*, a substance closely resembling picric acid; it forms *compounds* with naphthalene (pale yellow needles, m. p. 125—130°), with anthracene (ruby-red needles, m. p. 164—165°), and yellow precipitates with alkaloids. The *strychnine* and *cinchonine* salts were analysed.

With phosphorus pentachloride, the phenol gives 1-*chloro*-2-*cyano*-4 : 6-*dinitrobenzene*, which forms yellow crystals melting at 139°, and with aniline yields 2-*cyano*-4 : 6-*dinitrodiphenylamine*,

$$CN\cdot C_6H_2(NO_2)_2\cdot NHPh;$$

the latter crystallises in yellow needles melting at 183°. With sodium sulphide, *dicyanotetranitrophenyl sulphide* is obtained as yellow crystals melting at 238°. K. J. P. O.

Aromatic Derivatives of Sulphur. By J. J. Blanksma (*Rec. Trav. Chim.*, 1901, **20**, 399—410. Compare Abstr., 1901, i, 264, and preceding abstract).—*o-Nitrophenyl mercaptan*, $NO_2\cdot C_6H_4\cdot SH$, prepared by the action of sodium sulphide on *o*-chloronitrobenzene, melts at 45°, and is oxidised by the air to 1 : 1′-dinitrodiphenyl disulphide (m. p. 195°). 4-*Chloro-2-nitrophenyl mercaptan*, $NO_2\cdot C_6H_3Cl\cdot SH$, forms yellow crystals melting at 122°, and by iodine in alcoholic solution is readily converted into the *disulphide* melting at 212° (compare Beilstein and

Kurbatoff, Abstr., 1879, 230); 4-*bromo-2-nitrophenyl mercaptan* forms yellow crystals melting at 110°, and is oxidised by the air or by iodine into 4 : 4′-*dibromo-2* : 2′-*dinitrophenyl sulphide*, $S(C_6H_3Br\cdot NO_2)_2$, melting at 165°. By nitric, acid the latter is converted into the *sulphoxide*, $SO(C_6H_3Br\cdot NO_2)_2$, which melts at 238°.

p-Nitrophenyl mercaptan condenses with benzaldehyde in the presence of hydrochloric acid, yielding a *mercaptal*, $CHPh(S\cdot C_6H_4\cdot NO_2)_2$, which forms yellow crystals melting at 152°.

p-*Nitrophenyl methyl mercaptole*, $NO_2\cdot C_6H_4\cdot SMe$, prepared from sodium *p*-nitrothiophenoxide and methyl iodide, melts at 67° and has a pleasant odour; the corresponding *ethyl* compound melts at 40°. 4-*Chloro-2-nitrophenyl methyl mercaptole* melts at 128°, and the corresponding *bromo*-derivative at 126°.

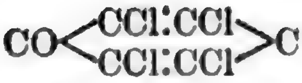
Sodium *o*-nitrothiophenoxide, and 1-bromo-2 : 4-dinitrobenzene yield a *sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot C_6H_3(NO_2)_2$, as yellow crystals, melting at 131°; similarly, an isomeric *sulphide*, melting at 155°, is obtained from sodium *p*-nitrothiophenoxide and 1-chloro-2 : 4-dinitrobenzene; from sodium 4-bromo-2-nitrothiophenoxide and 1-chloro-2 : 4-dinitrobenzene is formed 4-*bromo*-2 : 2′ : 4′-*trinitrophenyl sulphide* melting at 142°. With nitric acid, the latter gives a *sulphoxide* melting at 220°. In a similar manner were prepared 4-*chloro*-2 : 2′ : 4′-*trinitrophenyl sulphide*, (m. p. 141°) and 4-*bromo*-2 : 2′-*dinitrophenyl sulphide* (m. p. 131°). From the sodium derivative of thiofluorescein and 1-chloro-2 : 4-dinitrobenzene is obtained *fluorescein* 2 : 4-*dinitrophenyl sulphide* as yellow crystals melting at 168°.

In an analogous manner, chloro- (or bromo-)dinitrobenzene reacts with potassium xanthate, forming a dinitrophenyl ester of xanthic acid, which immediately decomposes into a dinitrophenyl mercaptan, carbon oxysulphide, and ethyl alcohol; the mercaptan then reacts with the excess of chlorodinitrobenzene, yielding tetranitrophenyl sulphide. K. J. P. O.

[4-Nitro-2-aminophenol-6-sulphonic Acid.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 123611).—4-*Nitro*-2-*aminophenol*-6-*sulphonic acid* (*Acid "III"*), obtained by reducing 2 : 4-dinitrophenol-6-sulphonic acid with a solution of sodium sulphide and potassium hydroxide, and decomposing the resulting potassium salt with a mineral acid, crystallises in greyish-brown leaflets and decomposes at 285° with slight explosion. The *mono*- and *di-potassium* salts are crystalline, and the *diazo*-compound is very stable. G. T. M.

Action of Bromine and Chlorine on Phenols: Substitution Products: ψ-Bromides and ψ-Chlorides. By THEODOR ZINCKE (*Annalen*, **320**, 145—178. Compare Abstr., 1899, i, 265).—A theoretical discussion bearing on the three succeeding abstracts and on work already published (compare Abstr., 1898, i, 70; 1899, i, 265, 616). G. T. M.

Action of Bromine on Tetrachloro-*p*-cresol: Tetrachloro-*p*-cresol ψ-Bromide and its Transformation Products. By THEODOR ZINCKE and K. WIEDERHOLD (*Annalen*, 1902, **320**, 179—198). —*Tetrachloro*-p-*cresol* ψ-*bromide* (*tetrachloro*-p-*hydroxybenzyl bromide*),


$\mathrm{CO}\left<\begin{matrix}\mathrm{CCl{:}CCl}\\ \mathrm{CCl{:}CCl}\end{matrix}\right>\mathrm{CH\cdot CH_2Br}$, or $\mathrm{OH\cdot C_6Cl_4\cdot CH_2Br}$, prepared by heating tetrachloro-*p*-cresol and bromine in sealed tubes at 100°, crystallises in lustrous, white needles and melts at 159—160°; it is reduced to tetrachloro-*p*-cresol by zinc and hydrochloric acid, whilst it dissolves in warm alkali hydroxide solution with loss of hydrogen bromide.

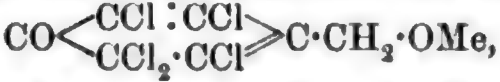
Tetrachloro-p-*hydroxybenzyl alcohol*, $\mathrm{OH\cdot C_6Cl_4\cdot CH_2\cdot OH}$, results from the addition of water to an acetone solution of the preceding substance; it crystallises from benzene or acetone in lustrous needles decomposing at 187—188°, and dissolves in solutions of alkali carbonates and hydroxides; its *diacetyl* derivative, $\mathrm{OAc\cdot C_6Cl_4\cdot CH_2\cdot OAc}$, crystallises from light petroleum in white needles melting at 120°. The ψ-bromide yields its *acetyl* derivative, $\mathrm{OAc\cdot C_6Cl_4\cdot CH_2Br}$, with acetic anhydride and the *monoacetyl* derivative, $\mathrm{O{:}C_6HCl_4\cdot CH_2\cdot OAc}$ or

$$\mathrm{OH\cdot C_6Cl_4\cdot CH_2\cdot OAc},$$

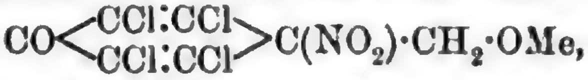
of the preceding alcohol with acetic acid and sodium acetate; the former of these crystallises in nacreous leaflets melting at 128°, the latter in white needles melting at 170°; both these compounds yield the preceding diacetyl derivative when heated with acetic anhydride and sodium acetate.

The *nitro-ketone*, $\mathrm{O{:}C_6Cl_4(NO_2)\cdot CH_2\cdot OH}$, of tetrachloro-*p*-hydroxybenzyl alcohol, produced by adding nitric acid of sp. gr. 1·4 to a glacial acetic acid solution of the alcohol, is an unstable, white, amorphous substance decomposing at 140°; it is converted into chloranil by hot nitric acid.

Tetrachloro-p-*hydroxybenzyl methyl ether*, $\mathrm{OH\cdot C_6Cl_4\cdot CH_2\cdot OMe}$, obtained by boiling the ψ-bromide with methyl alcohol, separates from benzene in thick, white needles and melts at 152—153°; it dissolves in solutions of the alkali hydroxides and carbonates, is reconverted into the ψ-bromide by heating with bromine, yields a *keto-chloride*,

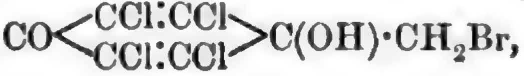

$$\mathrm{CO}\left<\begin{matrix}\mathrm{CCl{:}CCl}\\ \mathrm{CCl_2\cdot CCl}\end{matrix}\right>\mathrm{C\cdot CH_2\cdot OMe},$$

with chlorine in glacial acetic acid, and a *nitro-ketone*,

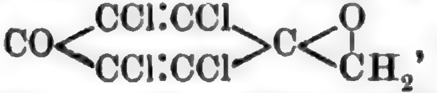

$$\mathrm{CO}\left<\begin{matrix}\mathrm{CCl{:}CCl}\\ \mathrm{CCl{:}CCl}\end{matrix}\right>\mathrm{C(NO_2)\cdot CH_2\cdot OMe},$$

with nitric acid; the former derivative separates in monoclinic crystals melting at 70—72°, the latter is a yellowish-white precipitate decomposing at 140°.

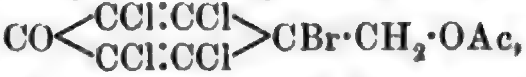
Tetrabromohydroxytoluketone (*tetrachlorobromotoluquinol*),


$$\mathrm{CO}\left<\begin{matrix}\mathrm{CCl{:}CCl}\\ \mathrm{CCl{:}CCl}\end{matrix}\right>\mathrm{C(OH)\cdot CH_2Br},$$

results from the action of nitric acid of sp. gr. 1·4 and separates from benzene in stout, colourless needles melting at 163—164°; its *acetyl* derivative, $\mathrm{O{:}C_6Cl_4(OAc)\cdot CH_2Br}$, prepared with acetyl chloride, forms colourless leaflets and melts at 143—144°; the hydroxy-ketone and its acetyl compound on reduction both yield tetrachloro-*p*-cresol.

The *compound* 
$\mathrm{CO}\left<\begin{matrix}\mathrm{CCl{:}CCl}\\ \mathrm{CCl{:}CCl}\end{matrix}\right>\mathrm{C}\left<\begin{matrix}\mathrm{O}\\ |\\ \mathrm{CH_2}\end{matrix}\right.$, obtained by treating the hydroxy-ketone with alcoholic sodium hydroxide, crystallises from benzene or alcohol in colourless needles melting at 165—166°. This

substance reacts with acetyl bromide, yielding the *compound*



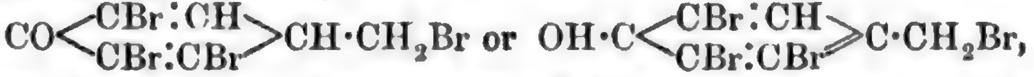
$$\mathrm{CO}<\begin{matrix}\mathrm{CCl{:}CCl}\\\mathrm{CCl{:}CCl}\end{matrix}>\mathrm{CBr{\cdot}CH_2{\cdot}OAc},$$

melting at 105°, which is isomeric with the acetyl derivative of the hydroxy-ketone; the corresponding *chloro*-derivative melts at 106—108°; these products both crystallise in lustrous, white leaflets.

G. T. M.

Action of Bromine on *p*-Cresol: Substitution Products and ψ-Bromides of *p*-Cresol. By THEODOR ZINCKE and K. WIEDERHOLD (*Annalen*, 1902, **320**, 199—220).—*p*-Cresol, when dissolved in chloroform and treated with bromine, readily yields 3-bromo-*p*-cresol and 3 : 5-dibromo-*p*-cresol, the former being purified by distillation and the latter by crystallisation from alcohol. *Tribromo*-p-*cresol* results when the action is performed in the presence of powdered iron, the product being crystallised from glacial acetic acid or benzene; it separates in needles melting at 102°; its *acetyl* derivative forms thick, colourless needles and melts at 77°. *Tetrabromo*-p-*cresol*, obtained by heating the preceding compound with bromine and crystallising the product from glacial acetic acid, forms thick, lustrous needles melting at 196°, the sodium salt separates in quadratic leaflets and the *acetyl* derivative in lustrous, colourless needles melting at 156°.

[With FR. WAGNER in part.] *Tribromo*-p-*cresol ψ-bromide* (*tribromo*-p-*hydroxybenzyl bromide*),



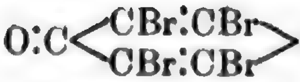
$$\mathrm{CO}<\begin{matrix}\mathrm{CBr{:}CH}\\\mathrm{CBr{:}CBr}\end{matrix}>\mathrm{CH{\cdot}CH_2Br}\ \text{or}\ \mathrm{OH{\cdot}C}<\begin{matrix}\mathrm{CBr{:}CH}\\\mathrm{CBr{:}CBr}\end{matrix}>\mathrm{C{\cdot}CH_2Br},$$

prepared by heating tribromo-*p*-cresol with bromine in sealed tubes at 100°, crystallises from ether, benzene, or glacial acetic acid in colourless needles melting at 122°; it is insoluble in cold aqueous alkali hydroxides, but is decomposed by these reagents on warming. The substance is reduced to tribromo-*p*-cresol by zinc and hydrochloric acid and yields *tribromo*-p-*hydroxybenzyl alcohol*, $OH{\cdot}C_6HBr_3{\cdot}CH_2{\cdot}OH$, when treated with water in acetone solution; the product crystallises from benzene in colourless needles melting at 138° and decomposing at 200°. It is soluble in sodium hydroxide solution and is reconverted into the ψ-bromide by hydrogen bromide dissolved in glacial acetic acid.

The *diacetyl* derivative, $OAc{\cdot}C_6HBr_3{\cdot}CH_2{\cdot}OAc$, crystallises from benzene in colourless needles melting at 107°; the *monoacetyl* derivative, $O{:}C_6H_2Br_3{\cdot}CH_2{\cdot}OAc$ or $OH{\cdot}C_6HBr_3{\cdot}CH_2{\cdot}OAc$, obtained by heating the ψ-bromide with acetic acid and sodium acetate, forms rhombic plates and melts at 123°. The ψ-bromide, when heated with acetic anhydride, yields its *acetyl* derivative, $OAc{\cdot}C_6HBr_3{\cdot}CH_2Br$, a substance forming needles melting at 116°. These two acetyl derivatives, when heated with glacial acetic acid and fused sodium acetate, both give rise to the preceding diacetyl compound.

Tribromo-p-*hydroxybenzyl methyl ether*, $OH{\cdot}C_6HBr_3{\cdot}CH_2{\cdot}OMe$, produced by heating the ψ-bromide with methyl alcohol, crystallises from benzene in colourless needles and melts at 72°; the *acetyl* compound melts at 60°.

Tetrabromo-p-*cresol ψ-bromide* (*tetrabromo*-p-*hydroxybenzyl bromide*),

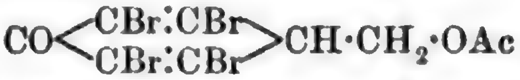

$\mathrm{O{:}C}<\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}>\mathrm{CH{\cdot}CH_2Br}$ or $OH{\cdot}C_6Br_4{\cdot}CH_2Br$, formed by heating tribromo-*p*-cresol for 4 hours with excess of bromine in sealed tubes at 100°, crystallises from glacial acetic acid in lustrous needles and from benzene in white leaflets; it melts at 182°; its acetyl derivative, $OAc{\cdot}C_6Br_4{\cdot}CH_2Br$, obtained by the action of boiling acetic anhydride, separates from the ordinary organic solvents in nacreous leaflets melting at 171—172°.

*Tetrabromo-*p*-hydroxybenzyl alcohol*, $OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}OH$, produced by adding water to the acetone solution of the preceding ψ-bromide, crystallises from this solvent or from benzene in lustrous needles, sublimes above 200°, and decomposes at 250°; it is soluble in solutions of the alkali hydroxides and carbonates, zinc and hydrochloric acid reduce it to tetrabromo-*p*-cresol, whilst hydrogen bromide in glacial acetic acid or methyl alcohol regenerates the ψ-bromide. The *diacetyl* derivative, $OAc{\cdot}C_6Br_4{\cdot}CH_2{\cdot}OAc$, forms white, silky needles and melts at 154—156°.

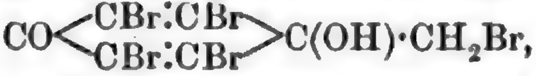
*Tetrabromo-*p*-hydroxybenzyl methyl ether*, $OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}OMe$, results from the action of boiling methyl alcohol on the ψ-bromide; it crystallises in slender needles, melts at 144°, and dissolves in solutions of the alkali hydroxides and carbonates; its *acetyl* derivative,

$$OAc{\cdot}C_6Br_4{\cdot}CH_2{\cdot}OMe,$$

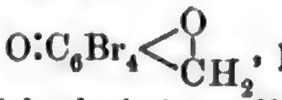
forms white needles and melts at 177—178°.

The *monoacetyl* derivative, 
$\mathrm{CO}<\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}>\mathrm{CH{\cdot}CH_2{\cdot}OAc}$ or $OH{\cdot}C_6Br_4{\cdot}CH_2{\cdot}OAc$, of tetrabromo-*p*-hydroxybenzyl alcohol, produced by heating the ψ-bromide with glacial acetic acid and sodium acetate, crystallises in needles and melts at 159—160°; it is converted into the diacetyl compound by acetic anhydride.

Pentabromohydroxytoluketone (*pentabromotoluquinol*),


$$\mathrm{CO}<\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}>\mathrm{C(OH){\cdot}CH_2Br},$$

obtained by warming the tetrabromo-ψ-bromide with nitric acid of sp. gr. 1·4, separates from the ordinary organic solvents in prismatic crystals or rhombohedra and melts at 195°; it is reduced by zinc and hydrochloric acid to tetrabromo-*p*-cresol and yields a characteristic anilide; its *acetyl* derivative, $O{:}C_6Br_4(OAc){\cdot}CH_2Br$, produced by means of acetyl chloride or bromide, crystallises in lustrous needles and melts at 175—176°.

The *compound* 
$\mathrm{O{:}C_6Br_4}<\begin{matrix}\mathrm{O}\\ |\\ \mathrm{CH_2}\end{matrix}$, prepared by treating the preceding hydroxy-ketone with alcoholic sodium hydroxide solution, crystallises in needles from acetone and in leaflets from glacial acetic acid and decomposes at 197—198°; it is insoluble in aqueous solutions of the alkali hydroxides, but dissolves in the alcoholic alkaline solution; its anilide crystallises in lustrous, brown leaflets. G. T. M.

Tribromo-4-hydroxy-*m*-xylene ψ-Dibromide. By THEODOR ZINCKE and E. TRIPP (*Annalen*, 1902, **320**, 220—231. Compare Auwers and Ziegler, Abstr., 1897, i, 33).—Tribromo-4-hydroxy-*m*-xylene ψ-dibromide (pentabromo-4-hydroxy-*m*-xylene) is readily prepared by heating tribromo-4-hydroxy-*m*-xylene and bromine in sealed tubes at 100°; it has a constitution represented either by $O\colon C_6HBr_3(CH_2Br)_2$ or $OH\cdot C_6Br_3(CH_2Br)_2$, for it contains two readily exchangeable bromine atoms. The *monoacetyl* derivative,

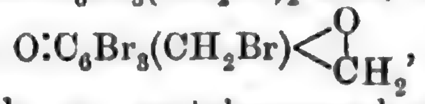
$$OH\cdot C_6Br_3(CH_2\cdot OAc)\cdot CH_2Br,$$

obtained by the action of hot glacial acetic acid and silver acetate on the ψ-dibromide, crystallises in white, felted needles and melts at 148—152°; the diacetyl derivative, $OH\cdot C_6Br_3(CH_2\cdot OAc)_2$, melts at 170° (Auwers gives 172°); the *triacetyl* compound, $OAc\cdot C_6Br_3(OAc)_2$, forms rhombohedral crystals melting at 98—99°. The acetyl derivative, $OAc\cdot C_6Br_3(CH_2Br)_2$, of the ψ-dibromide, obtained by the action of acetic anhydride, melts at 178—179°.

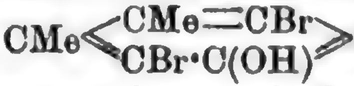
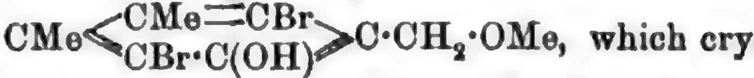
*Pentabromo-*m*-hydroxyxyloketone* (*pentabromo-*m*-xyloquinol*),

$$O\colon C_6Br_3(CH_2Br)_2\cdot OH,$$

produced by treating the pentabromide with nitric acid of sp. gr. 1·4, crystallises in colourless prisms and melts at 182°; it is reduced to tribromo-4-hydroxy-*m*-xylene by zinc and hydrobromic acid; its *acetyl* derivative, $O\colon C_6Br_3(CH_2Br)_2\cdot OAc$, forms needles melting at 158°.

The *compound*  $O\colon C_6Br_3(CH_2Br){<}\begin{matrix}O\\|\\CH_2\end{matrix}$, resulting from the action of sodium hydroxide on pentabromo-*m*-hydroxyxyloketone, crystallises from the ordinary organic solvents in pale yellow, silky needles; its *additive* product, $O\colon CBr_4(CH_2Br)\cdot CH_2\cdot OAc$, with acetyl bromide, crystallises from glacial acetic acid in lustrous, white leaflets and melts at 142°. G. T. M.

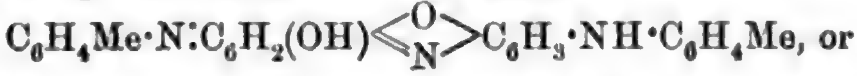
s-Trinitroxylenol. By J. J. Blanksma (*Rec. Trav. Chim.*, 1901, **20**, 422—424).—*s-Trinitroxylenol*, $C_6Me_2(NO_2)_3\cdot OH$, is prepared by the action of fuming nitric acid on *s*-xylenol; it crystallises in colourless needles melting at 104°, and resembles picric acid very closely, but does not react with potassium cyanide. K. J. P. O.

Third Tribromide of ψ-Cumenol. By O. Anselmino (*Ber.*, 1902, **35**, 795—798. Compare Abstr., 1899, i, 34, and this vol., i, 214).—*Dibromo-o-hydroxy-ψ-cumyl bromide*,  $CMe{<}\begin{matrix}CMe{=}CBr\\CBr\cdot C(OH)\end{matrix}{>}C\cdot CH_2Br$, is prepared by the action of bromine on bromo-*o*-hydroxy-ψ-cumyl bromide; it crystallises in needles melting at 119·5°, and is insoluble in alkali hydroxides. When boiled with methyl alcohol, it is converted into the corresponding *methyl ether* of dibromo-*o*-hydroxy-ψ-cumyl alcohol,  $CMe{<}\begin{matrix}CMe{=}CBr\\CBr\cdot C(OH)\end{matrix}{>}C\cdot CH_2\cdot OMe$, which crystallises in leaflets with a silvery lustre melting at 43°. When the bromide is treated with potassium iodide in acetic acid solution, *dibromo-o-hydroxy-ψ-cumyl iodide* is formed, crystallising in yellow needles melting at 124°. *Dibromo-o-hydroxy-ψ-cumyl acetate* is formed on treating an acetic acid solution of the bromide with zinc dust, and crystallises in lustrous prisms melting at 116°. K. J. P. O.

m-Hydroxyphenyl-p-tolylamine. By Robert Gnehm and Louis Veillon (*J. pr. Chem.*, 1902, [ii], **65**, 49—81).—*Acetyl-*m*-hydroxyphenyl-*p*-tolylamine*, $OH\cdot C_6H_4\cdot NAc\cdot C_6H_4Me$, obtained by the action of acetyl chloride or acetic anhydride on *m*-hydroxyphenyl-*p*-tolylamine, crystallises in quadratic tablets, melts at 213°, and dissolves sparingly in hot alcohol, ethyl acetate, or methyl alcohol, and more readily in glacial acetic acid; its *ethyl* ether, obtained by the action of ethyl iodide or ethyl sulphate on it, or by the action of acetyl chloride on *m*-ethoxyphenyl-*p*-tolylamine, crystallises in colourless, quadratic tablets and melts at 61°. The *barium* salt of the *disulphonic acid* of the acetyl derivative forms white needles containing $1H_2O$; the *barium* salt of the *trisulphonic acid* could not be obtained in a crystalline state.

By the sulphonation of *m*-hydroxyphenyl-*p*-tolylamine under varying conditions, mono-, di-, and tri-sulphonic acids were obtained. The *monosulphonic acid* crystallises in microscopic, quadratic tablets, and is slightly soluble in hot water; its *potassium*, *sodium*, and *barium* salts are described. The *disulphonic acid* forms an indistinctly crystalline mass; its *potassium*, *sodium*, and *barium* (with $1H_2O$) salts were prepared. The *barium* salt of the *trisulphonic acid* was obtained as a brownish powder. When the monosulphonic acid is heated with phthalic anhydride for 2 hours at 170°, the *disulphonic acid* of *s*-di-*p*-tolylrhodamine is produced; the same substance is obtained by the sulphonation of di-*p*-tolylrhodamine.

m-Hydroxyphenyl-*p*-tolylnitrosoamine melts at 127°. By the action of alcoholic hydrogen chloride at 0°, it is converted into the isomeric *nitroso*-m-*hydroxyphenyl*-p-*tolylamine*, $OH\cdot C_6H_3(NO)\cdot NH\cdot C_6H_4Me$, which crystallises in dark red needles, melts at 162·2°, and is easily soluble in alcohol, chloroform, or warm benzene; it is decomposed by sodium hydroxide with formation of *p*-toluidine and other products. When this compound is heated with a mixture of aniline and aniline hydrochloride, a *substituted azophenine*, $C_{31}H_{26}ON_4$, is produced, which crystallises from hot toluene in brown needles and melts at 190°. p-*Amino*-m-*hydroxyphenyl*-p-*tolylamine*, $NH_2\cdot C_6H_3(OH)\cdot NH\cdot C_6H_4Me$, obtained by reducing the nitroso-compound with ammonium sulphide, crystallises in lustrous, silver-grey leaflets which, on exposure to air, rapidly turn dark blue; it melts at 149°, and dissolves readily in alcohol or ether and sparingly in benzene; its *hydrochloride* and *sulphate* form dark needles. p-*Tolylamino*-m-*hydroxyphenyl*-μ-*cyanazomethine*-p-*nitrobenzene*, $C_6H_4Me\cdot NH\cdot C_6H_3(OH)\cdot N{:}C(CN)\cdot C_6H_4\cdot NO_2$, obtained by the action of *p*-nitrobenzyl cyanide on nitroso-*m*-hydroxyphenyl-*p*-tolylamine, crystallises in small, flat, red needles, melts at 152°, and is soluble in alcohol, ether, benzene, or toluene; the solution in benzene or toluene is strongly fluorescent. When nitroso-*m*-hydroxyphenyl-*p*-tolylamine is heated with *m*-hydroxyphenyl-*p*-tolylamine in presence of sulphuric acid, an oxazine *dye*,



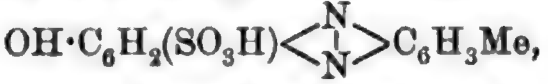
$$C_6H_4Me\cdot N{:}C_6H_2(OH)\genfrac{<}{>}{0pt}{}{O}{N}C_6H_3\cdot NH\cdot C_6H_4Me, \text{ or}$$

$$C_6H_4Me\cdot NH\cdot C_6H_2(OH)\genfrac{<}{>}{0pt}{}{O}{N}C_6H_3{:}N\cdot C_6H_4Me,$$

is produced, which crystallises in small, bluish-black needles, and is soluble in benzene, ether, alcohol, or glacial acetic acid; the *sulphate* is described.

m-*Hydroxyphenyl*-p-*tolylnitrosoaminesulphonic acid*,
$OH\cdot C_6H_3(SO_3H)\cdot N(NO)\cdot C_6H_4Me$,

obtained by the action of nitrous acid on *m*-hydroxyphenyl-*p*-tolylaminesulphonic acid, crystallises in lustrous, yellow, hexagonal plates, and is sparingly soluble in water or alcohol; the *sodium* and *potassium* salts form brown, rhombic crystals. Alcoholic hydrogen chloride converts it into p-*tolyl*-m-*hydroxyphenazinesulphonic acid*,



$$OH\cdot C_6H_2(SO_3H)<\overset{N}{\underset{N}{|}}>C_6H_3Me,$$

which forms a microcrystalline, violet-black powder, and is sparingly soluble in alcohol; its *barium* and *alkali* salts were prepared.

p-*Tolylamino*-m-*hydroxybenzyl alcohol*,

$$C_6H_4Me\cdot NH\cdot C_6H_3(OH)\cdot CH_2\cdot OH,$$

obtained by the action of formaldehyde (1 mol.) on *m*-hydroxyphenyl-*p*-tolylamine (1 mol.) in presence of hydrochloric acid (1 mol.), forms a yellow, amorphous powder and does not melt below 300°. If *m*-hydroxyphenyl-*p*-tolylamine (2 mols.) is heated with formaldehyde (1 mol.) and hydrochloric acid (2 mols.), *di*-p-*tolyldiaminodihydroxydiphenylmethane*, $C_{27}H_{26}O_2N_2$, is obtained as a grey, amorphous powder, which melts at 118° and is readily soluble in alcohol, acetone, ether, or chloroform; the *hydrochloride* melts at 213°. This substance is also produced when *p*-tolylamino-*m*-hydroxybenzyl alcohol reacts with *m*-hydroxyphenyl-*p*-tolylamine in presence of hydrochloric acid.

By the action of bromine on *m*-hydroxyphenyl-*p*-tolylamine, the *pentabromo*-derivative is produced, which crystallises in rhombic tablets of a pearly lustre, melts at 203—204°, and is sparingly soluble in the usual organic solvents. The *pentanitro*-derivative crystallises in reddish-brown, hexagonal prisms, melts at 230°, and dissolves readily in acetone, chloroform, or glacial acetic acid; it explodes on percussion or on heating. E. G.

Guaiacolsulphonic Acid. By HÄHLE (*J. pr. Chem.*, 1902, [ii], **65**, 95—96).—By the action of concentrated sulphuric acid on guaiacol, Tiemann and Koppe (Abstr., 1882, 54) obtained a mixture of two sulphonic acids, one of which yielded a crystalline potassium salt, whilst the other furnished a potassium salt which could only be obtained in a syrupy condition. The author considers that the latter was due to impurities in the guaiacol.

Guaiacolsulphonic acid may be prepared by leaving a mixture of guaiacol and sulphuric acid monohydrate for several hours at the ordinary temperature, or by the action of sulphuric acid on guaiacol carbonate; the *sodium* salt crystallises in colourless leaflets. E. G.

Action of Nitric Acid on Trichloro- and Tribromo-veratrole. By H. COUSIN (*Compt. rend.*, 1902, **134**, 290—291. Compare Abstr., 1900, i, 179, 487, and 1901, i, 82).—Trichloroveratrole is not attacked by ordinary nitric acid, but by fuming nitric acid is converted into *trichloronitroveratrole*, $NO_2\cdot C_6HCl_3(OMe)_2$, which crystallises in white, silky needles melting at 94—96°.

Tribromonitroveratrole, $NO_2\cdot C_6HBr_3(OMe)_2$, prepared by the action of fuming nitric acid on tribromoveratrole, crystallises in lustrous, faintly yellow needles melting at 115—116°. K. J. P. O.

Condensation of Acetylenic Hydrocarbons with Aldehydes; Synthesis of Secondary Alcohols with an Acetylenic Linking. By CHARLES MOUREU and HENRI DESMOTS (*Compt. rend.*, 1902, **134**, 355—357. Compare Abstr., 1901, i, 442).—When an aldehyde dissolved in ether is added to a molecular proportion of the sodium derivative of an acetylenic hydrocarbon suspended in ether, condensation readily takes place with production of a new class of secondary alcohols of the type $CR\vdots C\cdot CHR'\cdot OH$. They form insoluble compounds with mercuric chloride in aqueous solution, and reduce ammoniacal silver nitrate with production of a mirror, but have no action on an alcoholic solution of silver nitrate.

The following alcohols were prepared in this way: *a-Phenyl-β-heptinyl alcohol*, $CH_3\cdot[CH_2]_3\cdot C\vdots C\cdot CHPh\cdot OH$, which boils at 164—165° under 14 mm. pressure; *trichloromethyl-β heptinylcarbinol*,

$$CH_3\cdot[CH_2]_4\cdot C\vdots C\cdot CH(OH)\cdot CCl_3,$$

which boils at 141·5—142° under 12 mm. pressure; sp. gr. 1·2308 at 0°; *a-phenyl-β-octinyl alcohol*, $CH_3\cdot[CH_2]_4\cdot C\vdots C\cdot CHPh\cdot OH$, which boils at 180—182° under 16 mm. pressure; sp. gr. 1·0031 at 0°; *a-furfuryl-β-octinyl alcohol*, $CH_3\cdot[CH_2]_4\cdot C\vdots C\cdot CH(OH)\cdot C_4OH_3$, which boils at 150—151° under 13 mm. pressure and melts at about −1°; sp. gr. 1·0176 at 0°; *trichloromethyl-β-octinylcarbinol*,

$$CH_3\cdot[CH_2]_5\cdot C\vdots C\cdot CH(OH)\cdot CCl_3,$$

which boils at 166° under 20 mm. pressure; sp. gr. 1·2018 at 0°; *furfuryl-β-octinylcarbinol*, $CH_3\cdot[CH_2]_5\cdot C\vdots C\cdot CH(OH)\cdot C_4OH_3$, boiling at 163° under 13 mm. pressure; sp. gr. 1·004 at 0°; *phenylacetylenemethylcarbinol*, $CPh\vdots C\cdot CHMe\cdot OH$, boiling at 148—149° under 29 mm. pressure; sp. gr. 1·0431 at 0°; *phenylacetylenetrichloromethylcarbinol*, $CPh\vdots C\cdot CH(OH)\cdot CCl_3$, boiling at 183—184° under 18 mm. pressure; sp. gr. 1·3809 at 0°; *phenylphenylacetylenecarbinol*, $CPh\vdots C\cdot CHPh\cdot OH$, boiling at 220—222° under 20 mm. pressure; sp. gr. 1·116 at 0°; *furfurylphenylacetylenecarbinol*, $CPh\vdots C\cdot CH(OH)\cdot C_4OH_3$, boiling at 186—187° under 12 mm. pressure; sp. gr. 1·1601 at 0°.

C. H. B.

Electrolytic Oxidation of *p*-Toluic Acid. By HANS LABHARDT and R. ZSCHOCHE (*Zeit. Elektrochem.*, 1902, **8**, 93—96).—*p*-Toluic acid, dissolved in excess of sodium hydroxide, is oxidised electrolytically to terephthalic acid or carbon dioxide. The best current efficiency is obtained when a platinum anode is used. At small current densities (0·04 ampere per sq. cm.), terephthalic acid is the main product; as the current density is increased, further complete oxidation to carbon dioxide takes place to an increasing extent. T. E.

Ethyl Phenylglycine-*o*-carboxylates. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 122687).—Ethyl phenylglycine-*o*-carboxylate, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2Et$ (m. p. 145—150°), is conveniently prepared by the action of ethyl chloroacetate on anthranilic acid in the presence of alcohol and sodium acetate or sodium carbonate. The isomeric *ester*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H$, obtained by the action of chloroacetic acid on ethyl anthranilate, crystallises in needles melting at 167° (compare Abstr., 1900, i, 295). G. T. M.

Preparation of Indigotin. HUGO ERDMANN (D.R.-P. 123695).—*Anthranilidoacetonitrile* (ω-cyanomethylanthranilic acid) prepared by condensing together anthranilic acid, hydrogen cyanide, and formaldehyde, melts at 180° and forms *methyl ω-cyanomethylanthranilate*, $CO_2Me\cdot C_6H_4\cdot NH\cdot CH_2\cdot CN$, on treatment with methyl sulphate dissolved in methyl alcohol in the presence of sodium carbonate. The ester melts at 106·3°, and when heated at 160° with acetic anhydride and anhydrous sodium acetate, it yields *methyl acetyl-ω-cyanomethylanthranilate*, which crystallises in colourless needles and melts at 83°. The latter product, when mixed with naphthalene and heated at 150—170° with potassium hydroxide, yields a product which, when extracted with water, oxidised by a current of air, and acidified with hydrochloric acid, gives rise to indigotin, the colouring matter being thus obtained in a crystalline form. *Ethyl ω-cyanomethylanthranilate*, prepared either by substituting ethyl sulphate for the methyl ester in the production of its lower homologue, or by treating silver ω-cyanomethylanthranilate with ethyl iodide, melts at 89°; its *acetyl* derivative is oily, and may be employed in the preparation of indigotin.

G. T. M.

Crystallised Bismuth Salicylate and Gallate. By PAUL THIBAULT (*Ann. Chim. Phys.*, 1902, [vii], **25**, 268—284. Compare Abstr., 1901, i, 593, 712).—The communication contains a full description of the preparation of crystallised bismuth salicylate and references to the older processes for obtaining the salt.

Bismuth gallate, $BiC_7H_7O_7$, prepared by adding crystallised gallic acid to hydrated bismuth oxide (compare Abstr., 1902, ii, 106) suspended in a small quantity of water, may be obtained in transparent, micaceous, yellow granules on allowing the reagents to remain in contact for 15 days.

The salt, which cannot be produced from the anhydrous bismuth oxide, dissolves in solutions of ammonia or the alkali hydroxides and carbonates with an appreciable rise of temperature; the product of the action of potassium hydroxide has the composition, $BiK_2C_7H_7O_7,2H_2O$, and a similar *sodium* compound has been obtained. This result confirms the belief that the bismuth compound is not a true gallate, but rather a bismuthogallic acid having the following constitution:

$$CO_2H\cdot C_6H_2(OH){<}\substack{O\\O}{>}Bi\cdot Bi{<}\substack{O\\O}{>}C_6H_2(OH)\cdot CO_2H,4H_2O.$$

In this respect the compound resembles bismuth lactate and differs from the corresponding salicylate, which behaves towards alkali hydroxides as a true bismuth salt.

The gallic acid compound is not attacked by cold dilute sulphuric acid, but is decomposed and charred by the concentrated acid.

G. T. M.

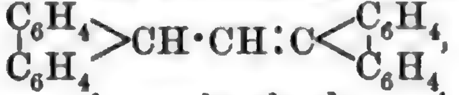
Aminosulphosalicylic Acids. JOSEPH TURNER (D.R.-P. 123115).—The nitrosalicylic acids, when boiled with solutions of sodium hydrogen sulphite, yield amino-sulphonic acids.

o-Aminosulphosalicylic acid, $NH_2\cdot C_6H_2(OH)(CO_2H)\cdot SO_3H$, a brownish-yellow powder, yields a soluble, greyish-white diazonium compound, and develops a yellowish-brown coloration with chromic acid.

p-*Aminosulphosalicylic acid* and its diazonium compound are far less soluble than the corresponding ortho-derivatives; the free acid develops a reddish-brown coloration with chromic acid. G. T. M.

Bimolecular Coumarone. By JOHANNES BOES (*Chem. Centr.*, 1902, i, 355; from *Apoth.-Zeit.*, 1902, **17**, 14. Compare Abstr., 1901, i, 31).—When the polymeride of coumarone $(C_8H_6O)_4$, which melts at 107—108°, is distilled under 20 mm. pressure, the fraction boiling at 230—240° on redistillation yields, not only thin, oily portions, which are stable, and acid oils, but also 1·5 per cent. of bimolecular coumarone $(C_8H_6O)_2$, which separates in crystals after the distillate has been kept for a long time. It melts at 99°, gives a carmine-red solution in sulphuric acid, and forms yellow nitro-derivatives, but is not attacked by hydrochloric acid or alkalis; a determination of the molecular weight gave 232. Attempts to convert the lower polymerides into the higher failed. Some clue to the mechanism of the process may possibly be more easily derived from experiments with coumarone or dicoumaryl. E. W. W.

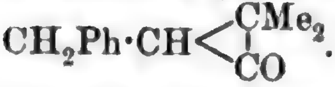
Ethyl Fluoreneoxalate. By WILHELM WISLICENUS and ALFRED DENSCH (*Ber.*, 1902, **35**, 759—765. Compare Abstr., 1900, i, 346).—The *phenylhydrazone* of fluoreneoxalic acid crystallises in slender, white needles and melts at 200—201°. The *oxime* of the ethyl ester crystallises from benzene and light petroleum and melts at 137—138°. Ethyl fluoreneoxalate, when treated with diazobenzene chloride, yields fluorenonephenylhydrazone, and when treated with methyl iodide and sodium methoxide, *ethyl methylfluoreneoxalate*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}{>}CMe\cdot CO\cdot CO_2Et$, which boils at 210—215° under 12 mm. pressure, and when hydrolysed yields *methylfluorene*, which crystallises in prisms and melts at 46—47°. *Ethylfluorene*, obtained in an analogous manner, melts at 107—108° and boils at 165—166° under 13 mm. pressure. Ethyl fluoreneoxalate is easily benzoylated, yielding a *compound*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}{>}C{:}C(OBz)\cdot CO_2Et$, which crystallises in long, yellow needles, melts at 141—142°, and, when treated with phenylhydrazine, yields benzoylphenylhydrazine and the phenylhydrazone of ethyl fluoreneoxalate. *p*-Nitrobenzoyl chloride, in the presence of sodium ethoxide, yields an analogous *compound*, which crystallises in yellow needles and melts at 188—189°. Ethyl formate, in the presence of sodium methoxide, slowly condenses with ethyl fluoreneoxalate, forming *methenylbisfluorene* (?),



$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}{>}CH\cdot CH{:}C{<}\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix},$$

which crystallises from toluene in slender, red needles and does not melt below 300°. R. H. P.

[Electrolytic Production of Benzaldehyde.] RICHARD NITHACK (D.R.-P. 123554).—An electrode composed of finely divided graphite and benzoic acid is employed as the cathode of a cell, the anode being of lead or platinum. The solution in the cell consists of 20 per cent. sulphuric acid saturated with benzoic acid. On passing through the cell an electric current of 1·5 amperes per sq. dcm. and 12—15 volts, benzaldehyde is produced, which forms an oily layer above the acid solution. G. T. M.

Condensation of Cinnamaldehyde with *iso*Butaldehyde. By Karl Michel and Karl Spitzauer (*Monatsh.*, 1901, **22**, 1119—1139).—When a mixture of cinnamaldehyde and *iso*butaldehyde is shaken with concentrated potassium carbonate solution, there is formed an aldol, $CHPh{:}CH\cdot CH(OH)\cdot CMe_2\cdot CHO$, which is a thick oil having a pleasant, fruity odour; it reduces alkaline silver solutions and forms an additive product with bromine. When heated, the aldol decomposes, but if rapidly distilled at 190—200° under 20 mm. pressure, a small amount passes over unchanged. It forms an aldoxime, $C_{13}H_{17}O_2N$, which is a thick oil decomposing on distillation under reduced pressure. On reduction, the aldol yields the corresponding *glycol*, $C_{13}H_{18}O_2$, a slightly yellow oil which decomposes on distillation. The glycol combines with bromine, and yields a *diacetate*. Under the influence of potassium hydroxide, cinnamaldehyde and *iso*butaldehyde react rapidly with the formation of the aldol and a *hydroxy acid*, $C_{13}H_{18}O_3$, which on liberation from the potassium salt forms a *lactone*, $C_{13}H_{16}O_2$; this distils, unchanged, at 343—345° under atmospheric pressure, melts at 89—90°, and does not form an additive product with bromine. The presence of excess of *iso*butaldehyde leads to the formation of octoglycol, whilst an increase in the proportion of potassium hydroxide increases the amount of the hydroxy-acid formed. The hydroxy-acid is also formed by the action of potassium hydroxide on the aldol. Oxidation of the acid by potassium permanganate in alkaline solution produces a dibasic acid, $C_{13}H_{16}O_4$, crystallising in short prisms which melt at 169°. When heated, the dibasic acid loses water at 210°, and is converted into an *anhydride* which distils at 243°, and, when crystallised from ether, forms four-sided prisms which melt at 111·5° and are converted into the acid on prolonged boiling with water. The constitution of the hydroxy-acid is probably $CH_2Ph\cdot CH(CO_2H)\cdot CMe_2\cdot CH_2\cdot OH$, and that of the dibasic acid $CH_2Ph\cdot CH(CO_2H)\cdot CMe_2\cdot CO_2H$. The latter, on distillation with lime, yields a substance which boils at 193—195°, and, on analysis, gives results agreeing with those required for the formula  $CH_2Ph\cdot CH<\begin{matrix}CMe_2\\ |\\ CO\end{matrix}$. The conversion of the aldol into the hydroxy-acid remains without explanation, and the properties of the dibasic acid do not agree with those of an acid to which Bischoff ascribes the same constitution (Abstr., 1891, 829). G. Y.

Condensation of Aromatic Aldehydes with Amines. By Otto Dimroth and Rudolf Zoeppritz (*Ber.*, 1902, **35**, 984—992).—The first reaction between an aromatic aldehyde or ketone and an aromatic amine consists in the addition of the elements of the amine to the carbonyl group, and the second in the removal of a mol. of water. With a few exceptions (Abstr., 1901, i, 378), it has hitherto been found impossible to isolate the intermediate additive products. It is now shown that these products may readily be isolated in the form of their hydrochlorides when the condensation occurs in the presence of aqueous hydrochloric acid, since the salts are much more stable than the bases themselves. The same salts are also produced when the benzylideneanilines are carefully treated with hydrochloric acid. It is found that the condensation between aldehydes and amines occurs much more readily and at lower temperatures when concentrated hydrochloric acid is present. The hydrochlorides thus produced vary considerably as regards their stability, those obtained from hydroxy-aldehydes being among the most stable. The corresponding free bases have been isolated, but in most cases show a great tendency to form the anhydrobenzylidene compounds.

Benzaldehydeaniline hydrochloride, $OH\cdot CHPh\cdot NHPh,HCl$, decomposes before it can be completely dried, as does also the corresponding *p*-toluidine compound. *Benzaldehyde-β-naphthylamine hydrochloride*, $OH\cdot CHPh\cdot NH\cdot C_{10}H_7,HCl$, forms yellow crystals, melts at 162—163°, and is readily decomposed by water; treatment with sodium carbonate solution at 0° converts it into benzylidene-*β*-naphthylamine.

*Benzaldehyde-*p*-nitroaniline hydrochloride*,

$$OH\cdot CHPh\cdot NH\cdot C_6H_4\cdot NO_2,HCl,$$

melts at about 188°, is insoluble in ether, but dissolves readily in alcohol and is decomposed by water at the ordinary temperature.

The corresponding base, $OH\cdot CHPh\cdot NH\cdot C_6H_4\cdot NO_2$, melts at 85—86° (compare Miller and Plöchl, Abstr., 1892, 1195; Hantzsch and Schwab, *ibid.*, 1901, i, 378).

Salicylaldehydeaniline hydrochloride, $OH\cdot C_6H_4\cdot CH(OH)\cdot NHPh,HCl$, melts at 93—94°; the *base* melts at 48° and readily loses water, yielding *o*-hydroxybenzylideneaniline.

p-*Hydroxybenzaldehydeaniline hydrochloride* may be crystallised from warm 20 per cent. hydrochloric acid and forms yellow needles melting at 215—217°. The *platinichloride* crystallises in dark yellow needles melting at 208—210°. The base melts at 170—175° and gradually loses water, yielding *p*-hydroxybenzylideneaniline.

Phenyliminobenzophenone melts at 116°, and not at 112—113° (Graebe, *Ber.*, 1899, **32**, 1680) and dissolves in concentrated hydrochloric acid, yielding crystals of *benzophenoneaniline hydrochloride*, $OH\cdot CPh_2\cdot NHPh,HCl$, melting at 191—194°; it is immediately decomposed by water into benzophenone and aniline.

2 : 4′-*Diacetoxybenzophenoneaniline hydrochloride*,

$$OAc\cdot C_6H_4\cdot C(OH)(NHPh)\cdot C_6H_4\cdot OAc,HCl,$$

is the compound previously described by Graebe as the corresponding anhydro-compound. J. J. S.

Synthesis of Aromatic Hydroxyaldehydes. By Otto Dimroth and Rudolf Zoeppritz (*Ber.*, 1902, **35**, 993—997. Compare Gattermann, Abstr., 1898, i, 581; 1899, i, 372).—Phosphorus oxychloride reacts with an ethereal solution containing molecular amounts of formanilide and resorcinol, yielding *resorcinaldehydeaniline hydrochloride*, $C_6H_3(OH)_2\cdot CH(OH)\cdot NHPh,HCl$, in the form of small, yellowish needles.

It crystallises from dilute hydrochloric acid in rhombic prisms, melts and decomposes at 140—141°, and dissolves readily in alcohol, but is insoluble in benzene or ether. The *base*, $C_6H_3(OH)_2\cdot CH(OH)\cdot NHPh$, forms yellow crystals, melts at 110°, and in a vacuum over sulphuric acid loses water and yields the anhydro-compound, *dihydroxybenzylideneaniline*, $C_6H_5(OH)_2\cdot CH{:}NPh$. This melts at 125—126°, is readily soluble in alcohol or ether, and is converted into the original hydrochloride when warmed with 18 per cent. hydrochloric acid.

Resorcylaldehyde may be obtained by boiling the crude condensation product, containing both phosphoric acid and ether, with 3 per cent. sodium hydroxide solution.

Pyrogallolaldehydeaniline hydrochloride,

$$C_6H_2(OH)_3\cdot CH(OH)\cdot NHPh,HCl,2H_2O,$$

crystallises in yellow, prismatic needles with a bluish-violet lustre, melts at 233—234°, and is readily soluble in alcohol. The *platinichloride* melts at 224—226°. The *base*, $C_6H_2(OH)_3\cdot CH(OH)\cdot NHPh$, obtained by dissolving the hydrochloride in sodium acetate solution, crystallises in small prisms melting at 179—180°, and readily loses water, yielding 1:2:3-*trihydroxybenzylideneaniline* melting at 194—195°.

The original hydrochloride is readily decomposed when boiled with alkalis in a stream of hydrogen yielding pyrogallolaldehyde.

J. J. S.

Nitro- and Amino-acetophenone (Hypnone). By Rudolf Camps (*Arch. Pharm.*, 1902, **240**, 1—18).—Acetophenone was added gradually to nitric acid of sp. gr. 1·51 free from nitrous fumes, the temperature not being allowed to rise above −8°. After a quarter-of-an-hour the solution was poured on to ice. Some crude *m*-nitroacetophenone separated and was filtered off; the mother liquor was neutralised at once with sodium carbonate and, finally, hydroxide, and extracted with ether, whereby crude *o*-nitroacetophenone was obtained. This extraction of the mother liquor is important, as one-third of the total yield (of 95 per cent.) was obtained in this way; previous workers have omitted this operation. The crude meta-compound was freed from admixed isomeride by continued suction; the crude ortho-compound by prolonged cooling at 0°, when some of the meta-isomeride crystallised out. Even after repeated fractionation, however, the oil still contained about 10 per cent. of the meta-compound.

Complete elimination of the meta-isomeride can best be effected after reduction; this was done with tin and hydrochloric acid, and the *o*-aminoacetophenone was distilled over with steam, the meta-compound, together with a little of the para-isomeride, remaining behind. *m*-Nitroacetophenone can be reduced in the same way; there is no need to precipitate the tin with hydrogen sulphide, for the bulk of the base can be precipitated as the stannichloride by adding excess of hydrochloric acid, and set free again by decomposing the precipitate with excess of sodium hydroxide, whilst the mother liquor can be concentrated, mixed with excess of sodium hydroxide, and extracted with ether. From 200 grams of acetophenone, there were obtained 145 of *m*- and 120 of *o*-nitroacetophenone; the latter was 90 per cent. pure, and yielded readily 75—80 grams of *o*-aminoacetophenone.

A little m-*nitrobenzoylformoxime*, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH{:}NOH$, is formed in the nitration, especially when this is carried out at 30—35°. It can be separated from the nitroacetophenones by means of its sparing solubility in ether. It melts at 152°, and yields *m*-nitrobenzoic and hydrocyanic acids when it is heated with aqueous alkalis. C. F. B.

s-Dimethyldiaminodi-*o*-tolyl Ketone. By ROBERT GNEHM and RALPH G. WRIGHT (*Ber.*, 1902, **35**, 913—915).—*Dimethyldiaminoditolyl ketone*, $C_{17}H_{20}ON_2$, crystallises from acetone in pale yellow needles and melts at 80—81°. The *hydrochloride*, $C_{17}H_{20}ON_2,2HCl$, crystallises from alcohol in flat, yellow prisms.

The *base* of auramine G (Gnehm and Schmid, American Patent No. 488430) forms yellow crystals and melts at 119—120°. The *picrate* crystallises from alcohol in glistening, orange-coloured needles and melts at 234°. The *sulphate* forms orange-coloured needles and melts at 182°. The *oxalate* is a yellow powder and melts at 210°.

The *hydrol*, prepared by reducing the ketone with sodium amalgam, crystallises from acetone in colourless needles, melts at 160—161°, and dissolves in acetic acid to a deep bluish-violet solution. With *p*-aminoazobenzene, it condenses to *benzeneazophenyl-leucauramine G*, $C_{29}H_{31}N_5$, which is precipitated from a solution in benzene by light petroleum in stout, orange-coloured tablets and melts at 170—170·5°. With benzeneazo-α-naphthylamine, *benzeneazo-α-naphthyl-leucauramine G*, $C_{33}H_{33}N_5$, is produced.

Leucauramine G, prepared by reducing auramine G with zinc dust and hydrochloric acid (Kern and Sandoz, D.R.-P. 64270) crystallises from benzene in yellow needles and melts at 207—208°.

By the action of hydrogen sulphide on a warm alcoholic solution of the hydrol, a colourless *thiohydrol* melting at 213—214° is produced. The *thio-ketone*, $C_{17}H_{20}N_2S$, from the auramine base and hydrogen sulphide, crystallises from alcohol in dull, blood-red crystals, melts at 176—177°, and forms two *hydrochlorides*, $C_{17}H_{20}N_2S,2HCl$ and $C_{17}H_{20}N_2S,HCl$, the former passing into the latter on exposure to the air. T. M. L.

Condensation of Methyl Ethyl Ketone with Benzaldehyde. By CARL D. HARRIES and G. HANS MÜLLER (*Ber.*, 1902, **35**, 966—971).—Benzaldehyde condenses with methyl ethyl ketone in the presence of sodium hydroxide, forming *benzylidenemethyl ethyl ketone*,

$$CHPh{:}CH \cdot COEt,$$

which crystallises from light petroleum in lustrous laminæ, melts at 38—39°, and boils at 142° under 12 mm. pressure. The *oxime* melts at 85—86° and the *phenylhydrazone* at 101°. When shaken with benzaldehyde, the ketone yields a white, crystalline *substance*, which melts at 65°, is probably a pyrone derivative, and forms an *oxime* melting at 195—196°. The *dibromo*-derivative crystallises in small needles and melts at 109—110°. When reduced, the ketone yields *α-benzylmethyl ethyl ketone*, which is also obtained by the distillation of a mixture of calcium propionate and hydrocinnamate. α-Benzylmethyl

ethyl ketone is a colourless, strongly refracting oil, which boils at 250—251° or at 128° under 17 mm. pressure, has n_D 1·50882 at 20°, and forms an oily *oxime* and *phenylhydrazone*. A *compound*, $C_{22}H_{26}O_2$, which crystallises in white needles melting at 168—169°, is also obtained as a bye-product in the reduction of the benzylidene-ketone.

In the presence of hydrogen chloride, benzaldehyde and methyl ethyl ketone condense to form *γ-benzylidene ethyl methyl ketone*,

$$CHPh:CMe{\cdot}COMe,$$

which crystallises from light petroleum in slender needles melting at 38° and boils at 127—130° under 12 mm. pressure. The *phenylhydrazone* crystallises from alcohol and melts at 105°. The *oxime* crystallises in large prisms melting at 103—104°, and the *dibromo*-derivative melts at 61°. When the benzylidene-ketone is reduced, a 60 per cent. yield of *γ-benzylethyl methyl ketone*, $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, and an oily *compound*, $C_{22}H_{26}O_2$, which boils at 190—210° under 8 mm. pressure are obtained; the ketone is an oil which boils at 234° or at 110—115° under 13 mm. pressure, and has n_D 1·50698 at 20°.

[Several of these compounds have been described by E. Levinstein (*Inaug. Diss. Berlin*)]. R. H. P.

Monohydroxybenzylidenebromoindanones. By K. MINIAT (*Bull. Soc. Chim.*, 1902, [iii], 27, 77—79).—The author has prepared a number of these compounds by the action of the hydroxybenzaldehydes on bromoindanone in presence of sodium hydroxide. o-*Hydroxybenzylidene-2-bromoindanone* is a pale red, crystalline substance which dissolves in hot dilute sodium hydroxide. Concentrated sulphuric acid colours the crystals red and yields an orange-coloured solution. The sodium salt crystallises in bright yellow needles which char at 220°. 2-*Bromo-o-acetoxyindanone*, obtained by boiling the *o*-hydroxybenzylidenebromoindanone with acetic anhydride and fused sodium acetate, crystallises from alcohol in colourless needles which melt at 142°. m-*Hydroxybenzylidene-2-bromoindanone* crystallises from alcohol in long, shining needles which melt at 239°; concentrated sulphuric acid colours the crystals orange and yields a yellow solution. m-*Acetoxybenzylidene-2-bromoindanone* is slightly soluble in alcohol and crystallises in colourless leaflets melting at 173—174°. p-*Hydroxybenzylidene-2-bromoindanone* is formed with greater difficulty than its two isomerides; it is best obtained by heating the alcoholic solution of *p*-hydroxybenzaldehyde and bromoindanone with fuming hydrochloric acid for a short time in a reflux apparatus. It crystallises in small, yellow needles which melt at 252°. Sulphuric acid colours the crystals red and yields a yellow solution. The *acetoxy*-derivative crystallises from glacial acetic acid in colourless needles melting at 226—227°. The author has also prepared compounds by the action of furfuraldehyde, cuminaldehyde, and cinnamaldehyde on bromoindanone. A. F.

Disulphones. IX. Derivatives of Unsaturated Ketones containing Sulphur. By THEODOR POSNER (*Ber.*, 1902, 35, 799—816. Compare Abstr., 1900, i, 5, 16; 1901, i, 14, 88, 474, 703).—The action of mercaptans on unsaturated ketones, which have one or two ethylene linkings in the β-position to the carbonyl group, has been investigated.

Benzylideneacetone and benzyl mercaptan, when treated with hydrogen chloride in acetic acid solution, yield *ββγ-trithiobenzyl-δ-phenylbutane*, $C_7H_7\cdot S\cdot CHPh\cdot CH_2\cdot CMe(SC_7H_7)_2$, which forms a viscous, pale yellow oil. On oxidation, with aqueous potassium permanganate, of a solution in carbon tetrachloride, *ββγ-tribenzylsulphone-δ-phenylbutane*, $C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot CMe(SO_2\cdot C_7H_7)_2$, is obtained as microscopic crystals melting at 112—113°.

ββγ-Trithioamyl-δ-phenylbutane, $C_5H_{11}\cdot S\cdot CHPh\cdot CH_2\cdot CMe(S\cdot C_5H_{11})_2$, prepared in a similar manner from amyl mercaptan and benzylideneacetone, is a mobile, pale yellow oil, and, on oxidation, does not yield a single sulphone.

Phenyl mercaptan and benzylideneacetone gave a mixture of mono- and tri-thiophenyl derivatives, which was oxidised to the sulphones. The latter were separated by crystallisation from water.

β-Phenylsulphone-β-phenylethyl methyl ketone,

$$SO_2Ph\cdot CHPh\cdot CH_2\cdot COMe,$$

crystallises in needles, soluble in water and melting at 115°; *ββγ-triphenylsulphone-δ-phenylbutane*, $SO_2Ph\cdot CHPh\cdot CH_2\cdot CMe(SO_2Ph)_2$, the insoluble sulphone, crystallises in short needles melting at 168°.

Mesityl oxide and benzyl mercaptan do not yield a single substance. Amyl mercaptan and mesityl oxide give a mixture of mono- and tri-thio-derivatives, from which, on oxidation, one sulphone, *β-amylsulphoneisobutyl methyl ketone*, $C_5H_{11}\cdot SO_2\cdot CMe_2\cdot CH_2\cdot COMe$, can be obtained in rhombic crystals melting at 71°.

Benzylideneacetophenone and benzyl mercaptan yield a mixture, from which, by oxidation, two sulphones can be obtained; these are separated by recrystallisation from alcohol. *β-Benzylsulphone-β-phenylethyl phenyl ketone*, $C_7H_7\cdot SO_2\cdot CHPh\cdot CH_2\cdot COPh$, melts at 147—148°; *ααγ-tribenzylsulphone-αγ-diphenylpropane*,

$$C_7H_7\cdot SO_2\cdot CHPh\cdot CH\cdot CPh(SO_2\cdot C_7H_7)$$

crystallises in lustrous needles melting at 217°.

Benzylideneacetophenone and amyl mercaptan give a mixture, on oxidation of which a sulphone, *β-amylsulphone-β-phenylethyl phenyl ketone*, $C_5H_{11}\cdot SO_2\cdot CHPh\cdot CH\cdot COPh$, is obtained melting at 142—143°. With phenyl mercaptan and the same ketone, *α-thiophenyl-β phenylethyl phenyl ketone*, $CH_2Ph\cdot CH(SPh)\cdot COPh$, is formed, crystallising in needles melting at 121°; on oxidation, it yields the corresponding *sulphone* melting at 160—161°. Dypnone and benzyl mercaptan yield a mixture of mercaptoles; on oxidation, *β-benzylsulphone-β-methyl-β-phenylethyl phenyl ketone*, $C_7H_7\cdot SO_2\cdot CMePh\cdot CH_2\cdot COPh$, is produced as a white, crystalline powder melting at 137—138°. From amyl mercaptan and dypnone is obtained an oily product yielding, on oxidation, *β-amylsulpho-β-methyl-β-phenylethyl phenyl ketone*, $C_5H_{11}\cdot SO_2\cdot CMePh\cdot CH_2\cdot COPh$, which crystallises in needles melting at 143—144°. From dypnone and phenyl mercaptan is formed *β-thiophenyl-β-methyl-β-phenylethyl phenyl ketone*, $SPh\cdot CMePh\cdot CH_2\cdot COMe$, as a viscous, dark-yellow oil, which, on oxidation, gives a crystalline powder, *β-phenylsulphone-β-*

methyl-β-phenylethyl phenyl ketone, $SO_2Ph\cdot CMePh\cdot CH_2\cdot COPh$, melting at 100°.

The substance previously described (Abstr., 1901, i, 474) as dibenzylideneacetonedisulphone (m. p. 140—142°) is now shown to be *dibenzylacetonediethylsulphone*, $CO(CH_2\cdot CHPh\cdot SO_2Et)_2$. Benzyl mercaptan and dibenzylideneacetone give a mixture of thio-derivatives, from the products of oxidation of which can be isolated *dibenzylacetonedibenzylsulphone*, $CO(CH_2\cdot CHPh\cdot SO_2\cdot C_7H_7)_2$, crystallising in needles melting at 185°. Amyl mercaptan and dibenzylideneacetone give *αγγε-tetrathioamyl-αε-diphenylpentane* as an oil; on oxidation, *dibenzylacetonediamylsulphone*, $CO(CH_2\cdot CHPh\cdot SO_2\cdot C_5H_{11})_2$, is obtained in small needles melting at 155°. Phenyl mercaptan and dibenzylideneacetone yield *dibenzylacetonedithiolphenyl*, $CO(CH_2\cdot CHPh\cdot SPh)_2$, crystallising in needles melting at 139—140°, which is oxidised to the corresponding *sulphone*, crystallising in needles melting at 166°.

The substance previously described as phoronedisulphone (m. p. 101°, *loc. cit.*) is now shown to be *di-β-ethylsulphoneisobutyl ketone*, $CO(CH_2\cdot CMe_2\cdot SO_2Et)_2$. Phorone and benzyl mercaptan yield *di-β-thiobenzylisobutyl ketone*, $CO(CH_2\cdot CMe_2\cdot SC_7H_7)_2$, as a pale yellow, mobile oil; this, on oxidation, is converted into the corresponding *disulphone*, which melts at 171—172°. With amyl mercaptan, phorone gives *di-β-thioamylisobutyl ketone*, $CO(CH_2\cdot CMe_2\cdot SC_5H_{11})_2$, as a pale yellow, mobile oil; the *disulphone* melts at 127—128°. With phenyl mercaptan, phorone yields *di-β-thiophenylisobutyl ketone*,

$$CO(CH_2\cdot CMe_2\cdot SPh)_2,$$

a mobile, yellow oil; the *disulphone* forms lustrous leaflets melting at 160°.

K. J. P. O.

Preparation of Deoxybenzoin. By HANS STOBBE (*Ber.*, 1902, **35**, 911—912).—A solution of benzoin in 90 per cent. alcohol is reduced by adding purified zinc and passing in hydrogen chloride. The solution is poured into water, heated for some hours, and the crude deoxybenzoin carefully dried and then distilled. The yield by this method is from 60 to 75 per cent. of the theoretical quantity.

T. M. L.

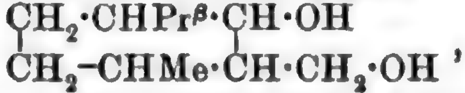
Hydroxylamino- and Nitroso-anthraquinone. I. By LEONHARD WACKER (*Ber.*, 1902, **35**, 666—669).—1-*Hydroxylaminoanthraquinone-2-sulphonic acid* is formed when 1:2-nitroanthraquinonesulphonic acid is reduced with dextrose and sodium hydroxide; the reddish-brown *sodium* salt, $C_{14}H_8O_6NSNa$, was isolated and analysed. In presence of strong sulphuric acid at 70—80°, the hydroxylamino-compound undergoes isomeric change and 1-*amino*-4-*hydroxyanthraquinone*-2-*sulphonic acid* is formed; the *sulphate* is yellow, but the *salts* are bluish-violet in alkaline solution and dye wool violet. 1-*Nitrosoanthraquinone*-2-*sulphonic acid* is formed on oxidising the hydroxylamino-compound with potassium ferricyanide; the *sodium* salt, $C_{14}H_6O_6NSNa$, forms minute, yellow, glistening flakes, and is only sparingly soluble in water.

T. M. L.

Derivatives of α-Aminoalizarin. By GUSTAV SCHULTZ and J. ERBER (*Ber.*, 1902, **35**, 906—908. Compare Roemer, Abstr., 1885, 1068).—Two isomeric compounds result from the action of acetic anhydride on α-aminoalizarin. When the base is mixed with sodium acetate and heated on a water-bath with acetic anhydride, a *diacetyl-α-aminoalizarin*, $C_{18}H_{13}O_6N$, is formed, which melts at 205° and crystallises unchanged from alcohol. When this compound, or the original base, is boiled with acetic anhydride, an *isomeride* is produced which forms reddish-brown flakes, melts at 245°, crystallises well from toluene, sublimes without decomposition, is hydrolysed by cold sodium hydroxide or by hot sodium carbonate, and when boiled with alcohol is converted into the isomeride melting at 205°.

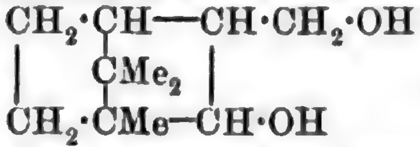
Benzoyl-α-aminoalizarin, $C_{21}H_{13}O_5N$, prepared by the action of benzoyl chloride on a solution of the base in boiling nitrobenzene, forms reddish-brown needles, is insoluble in ordinary solvents, but crystallises from nitrobenzene and sublimes with partial decomposition in brilliant red needles. *Dibenzoyl-α-aminoalizarin*, $C_{28}H_{17}O_6N$, separates from the mother liquors of the preceding compound in minute, brown needles, melts at 255°, and dissolves in chloroform, toluene, or nitrobenzene. *Dibenzoyl-β-alizarin* can be readily prepared by a similar method; it forms yellow, glistening flakes, melts at 252°, is highly pyroelectric, and crystallises well from chloroform or toluene. T. M. L.

Cyclic Dihydric Alcohols. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 123909).—*Menthyl glycol*,



produced by reducing hydroxymethylenementhone with sodium and hot ethyl or amyl alcohol, is an oil which solidifies on cooling, and consists of a mixture of two stereoisomerides. *cis*-Menthyl glycol passes into solution on extracting the preceding substance with ether and crystallises from light petroleum in lustrous prisms melting at 76—78° and boiling at 164—167° under 16 mm. pressure. *trans*-Menthyl glycol crystallises from benzene in lustrous leaflets and melts at 103—104°.

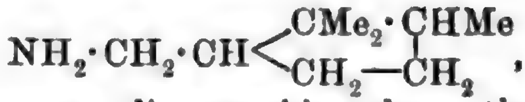
Camphyl glycol,

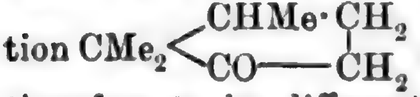


, prepared from hydroxymethylenecamphor, is a mixture of two isomerides, the *trans*-modification forming lustrous leaflets melting at 117—118°; the *cis*-compound, however, was not obtained pure. The crude glycol boils at 174—176° under 20 mm. pressure.

Hydroxymethylenedihydroisophorone yields the cis- and trans-*dihydroisophoryl glycols* the former crystallising in colourless leaflets melting at 103°, the latter forming a crystalline mass boiling at 170° under 17 mm. pressure. G. T. M.

Migration of the Methyl Group in the Molecule of Camphor. By EDMOND E. BLAISE and G. BLANC (*Bull. Soc. Chim.*, 1902, [iii], **27**, 71—76).—The authors claim to have proved that the α- and β-derivatives of camphor are not stereoisomeric.

Dihydro-α-aminocampholene,  $NH_2\cdot CH_2\cdot CH{<}\begin{matrix}CMe_2\cdot CHMe\\ CH_2-CH_2\end{matrix}$, is a colourless compound and has a more disagreeable odour than the β-derivative; it boils at 190°, has a specific rotation 32·48°, and a sp. gr. 0·8655 at 15°/15°. The *picrate* crystallises from dilute alcohol in large, yellow laminæ which melt and decompose at 227°. The *oxamide* forms long, silky needles melting at 147—148°. The *platinichloride* is very slightly soluble in water or alcohol, and when heated decomposes without melting. The *carbamide,* $C_9H_{17}\cdot NH\cdot CO\cdot NH_2$, forms slender needles very slightly soluble in cold benzene, and melts at 107—108°. In the preparation of the base, there is also formed the *ureide,* $C_8H_{15}\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot C_8H_{15}$. When the carbamide is heated, dihydro-α-campholenonitrile is formed, and by hydration with acids or alkalis, dihydro-α-campholenic acid.

By the bromination of α-dihydrocampholenic acid and subsequent esterification, *ethyl bromo-α-dihydrocampholenate,* $C_8H_{15}\cdot CHBr\cdot CO_2Et$, was obtained; it boils at 135—140° under 12 mm. pressure. The *unsaturated acid,* $C_8H_{14}\colon CH\cdot CO_2H$, obtained by the hydrolysis of the ester with alcoholic potash, readily crystallises from dilute alcohol or acetic acid in leaflets, melts at 70°, boils at 155° under 12 mm. pressure, is soluble in all organic solvents, absorbs bromine, and instantaneously decolorises alkaline permanganate. Adopting the α-constitution given by Mahla and Tiemann for dihydrocampholenic acid (compare Abstr., 1900, i, 507), the ketone formed by the oxidation must have the constitution  $CMe_2{<}\begin{matrix}CHMe\cdot CH_2\\ CO-CH_2\end{matrix}$ (4 : 5 : 5-trimethyl*cyclo*pentanone), and ought therefore to be different from the 2 : 3 : 3-trimethyl*cyclo*pentanone of Noyes (compare Abstr., 1900, i, 202). This the authors find to be the case. 4 : 5 : 5-*Trimethyl*cyclo*pentanone* is a colourless liquid with an odour both of camphor and of mint; it boils at 164—165°, and is insoluble in water. The *oxime* forms pearly scales, soluble in alcohol and in light petroleum, and melts at 107—108°. The *semicarbazone* forms small crystals insoluble in water, and very slightly soluble in cold, but more so in hot, alcohol, and melts at 188° without decomposition. The *benzylidene* derivative, $C_8H_{12}O\colon CHPh$, readily obtained by condensation in alkaline solution, crystallises in prisms which melt at 34° and are soluble in all organic solvents. A. F.

Action of Arsenic Acid on Pinene. By PAUL GENVRESSE (*Compt. rend.*, 1902, **134**, 360—362).—When pinene is distilled with about one-fortieth of its weight of crystallised arsenic acid, small quantities of terpinene, cymene, and terpineol are produced, but the chief product is a liquid identical with the original pinene in chemical and physical properties, except that its odour is somewhat different and its optical activity less, being only −26°16′ as compared with −40°51′ for the original pinene. If, however, the arsenic acid amounts to a quarter of the weight of the pinene, the greater part of the latter is readily converted into terpinene, together with some terpineol and a little cymene. This terpinene has a rotatory power of −10°21′ to −10°47′ in a 20 cm. tube. Limonene, when treated in the same way, is also converted into terpinene. C. H. B.

Algerian Oil of Rue. By HUGO VON SODEN and KARL HENLE (*Chem. Centr.*, 1902, i, 256; from *Pharm. Zeit.*, 1901, **46**, 1026—1027. Compare Abstr., 1901, i, 396).—The methyl heptyl ketone contained in Algerian oil of rue is the normal ketone, since, on oxidation, it yields normal octoic acid (caprylic acid), and by the action of phosphorus trichloride and ammonia it forms normal octamide (caprylamide); methyl heptyl ketoxime is also converted into normal heptylamine when treated with hot sulphuric acid by the Beckmann-Wallach method. The crude methyl heptyl ketoxime can be purified by distillation under reduced pressure, and then forms a clear liquid which boils at 108—109° under 6 mm. pressure, has a sp. gr. 0·882 at 20°, and solidifies at + 14°. Normal heptylamine boils at 153—156°; the picrate crystallises from a mixture of ether and light petroleum in yellow needles, and melts at 118·5—119·5°. The Algerian oil, like the ordinary oil, is slightly fluorescent; it contains 90 per cent. of admixed methyl heptyl ketone and methyl nonyl ketone, the amount of the former being twice as great as that of the latter, and to this larger proportion of methyl heptyl ketone its peculiar odour is mainly due.

The esters contained in the oil and boiling at about 200—210°, appear to consist, for the most part, of the acetates of the secondary alcohols corresponding with the ketones. E. W. W.

Essence of Ylang-ylang. By GEORGES DARZENS (*Bull. Soc. Chim.*, 1902, [iii], **27**, 83—85. Compare Abstr., 1895, i, 243, 294).—From the result of hydrolysis with aqueous potassium hydroxide, the author concludes that this essence probably contains methyl alcohol. He has also detected the presence of *p*-cresol, and confirmed the occurrence of benzoic and acetic acids already found by Reychler.

A. F.

Colophony. By WILHELM FAHRION (*Zeit. angew. Chem.*, 1902, **15**, 83—84. Compare this vol., i, 165).—Polemical. A reply to Dietrich and a *résumé* of Schkateloff's work (Abstr., 1889, 406). J. J. S.

Chlorophyll. VIII. Changes Undergone by Chlorophyll in passing through the Bodies of Animals. By EDWARD SCHUNCK (*Proc. Roy. Soc.*, 1902, **69**, 307—312).—Whilst the fæces of cows and sheep which have been fed exclusively on green vegetable food are found not to contain chlorophyll, certain derivatives of chlorophyll have been isolated therefrom. One of these appears to be phylloxanthin, and another, resembling phyllocyanin, is named by the author *scatocyanin*. The latter may be obtained by the extraction of dried cow dung with cold chloroform, and slow evaporation of the filtered solution, in the form of purplish-blue crystals with a brilliant metallic lustre. The substance is soluble in chloroform, boiling glacial acetic acid (fine crimson solution), concentrated sulphuric acid (grass-green to purplish-blue solution), boiling aniline (dull red solution), and alcoholic potash (yellow solution), but almost insoluble in boiling alcohol, ether, carbon disulphide, benzene, or aqueous potassium hydroxide. The absorption spectrum of the chloroform solution is nearly the same as that given by phyllocyanin; the absorption spectra of the glacial acetic and sulphuric acid solutions are also described. J. C. P.

Hydrazides and Azoimides of Organic Acids. XXVI. Hydrazide [and Azoimide] of Pyromucic Acid.

By THEODOR CURTIUS and ROBERT LEIMBACH (*J. pr. Chem.*, 1902, [ii], **65**, 20—41).—*Pyromucylhydrazide*, $C_4OH_3{\cdot}CO{\cdot}N_2H_3$, prepared by boiling ethyl pyromucate with hydrazine hydrate, crystallises in prisms, melting and becoming brown at 80° and boiling and decomposing at 279°; the *hydrochloride* crystallises in silky needles melting at 178°; the *sodium* derivative forms a crystalline mass. *Pyromucylacetylhydrazide*, $C_4OH_3{\cdot}CO{\cdot}N_2H_2{\cdot}COMe$, prepared from the hydrazide and acetic anhydride, crystallises in leaflets with a silky lustre, melting at 153·5°; *pyromucylbenzoylhydrazide*, prepared by boiling an alcoholic solution of the hydrazide, benzoyl chloride, and sodium hydroxide, crystallises in colourless leaflets melting at 226°. *Pyromucyl-β-propylidenehydrazide*, $C_4OH_3{\cdot}CO{\cdot}N_2H{:}CMe_2$, crystallises in colourless plates melting at 72°; *pyromucylbenzylidenehydrazide*,

$$C_4OH_3{\cdot}CO{\cdot}N_2H{:}CHPh,$$

in long needles, melting and decomposing at 219°. The *pyromucylhydrazide* of ethyl acetoacetate, $C_4OH_3{\cdot}CO{\cdot}N_2H{:}CMe{\cdot}CH_2{\cdot}CO_2Et$, forms colourless needles melting at 234°.

s-*Dipyromucylhydrazide*, $N_2H_2(CO{\cdot}C_4OH_3)_2$, prepared by the action of iodine on an alcoholic solution of the hydrazide, crystallises in small, lustrous needles melting at 232°.

Pyromucylazoimide, $C_4OH_3{\cdot}CO{\cdot}N_3$, prepared by adding sodium nitrite to a solution of the hydrazide in dilute acetic acid, crystallises in small, monoclinic plates melting at 62·5°. *Pyromucylanilide*,

$$C_4OH_3{\cdot}CO{\cdot}NHPh,$$

prepared from the azoimide and aniline in alcoholic solution, crystallises in colourless needles melting at 123·5°.

Ethyl furfurylcarbamate, $C_4OH_3{\cdot}NH{\cdot}CO_2Et$, prepared from the azoimide and boiling absolute alcohol, forms crystals, and boils at 133° under 24 mm. pressure and at 215° with decomposition under the ordinary pressure. *Methyl furfurylcarbamate*, $C_4OH_3{\cdot}NH{\cdot}CO_2Me$, from the azoimide and methyl alcohol, is a yellow oil boiling at 120° under 20 mm. pressure. *Difurfurylcarbamide*, $CO(NH{\cdot}C_4OH_3)_2$, prepared with difficulty by warming pyromucylazoimide with moist benzene, forms a yellow, crystalline mass, melting and decomposing at about 220°.

All attempts to prepare α-furfurylamine from the urethane failed.

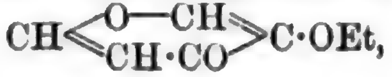
K. J. P. O.

Hydrolysis of Pyromucylurethane.

By R. MARQUIS (*Compt. rend.*, 1902, **134**, 288—289).—An account is given of preliminary and, at present, unsuccessful experiments on the formation of furfurylamine from pyromucylurethane by hydrolysis with alkalis (compare Leimbach, preceding abstract). K. J. P. O.

Ethylpyromeconyl Ether.

By RICCARDO OLIVERI-TORTORICI (*Gazzetta*, 1902, **32**, i, 56—62).—*Ethyl pyromeconyl ether*,

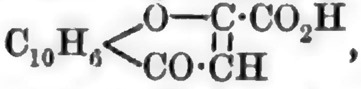
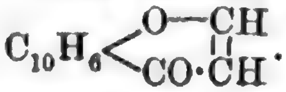


$$CH{\lessdot}\begin{matrix}O{-}CH{=}\\CH{\cdot}CO\end{matrix}{\gtrdot}C{\cdot}OEt,$$

obtained by heating ethylcomenic acid, forms a colourless, unstable liquid boiling at 220—221°, and giving no coloration with ferric chloride. It has a faint phenolic odour and a neutral reaction, and is soluble in most organic solvents. It is not attacked either by cold nitric acid or by a chloroform solution of bromine, but alkalis readily dissolve it, assuming an intense yellow colour. When hydrolysed in presence of alkalis, it is resolved quantitatively into formic acid and acetolic ether, $CH_2Ac\cdot OEt$. T. H. P.

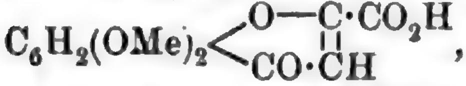
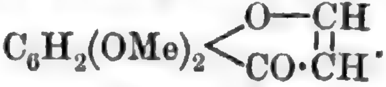
α-Naphthachromone. By Stanislaus von Kostanecki and G. Froemsdorff (*Ber.*, 1902, **35**, 859—861. Compare Abstr., 1901, i, 735).—*Ethyl* 1-*hydroxy*-2-*naphthoylpyruvate*,

$$OH\cdot C_{10}H_6\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et,$$

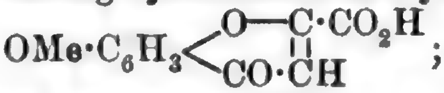
obtained by condensing 2-acetyl-α-naphthol with ethyl oxalate by means of sodium, crystallises from ethyl acetate in yellowish plates and melts at 114°; when boiled with concentrated hydrochloric acid, it yields *α-naphthachromonecarboxylic acid*,  $C_{10}H_6<\begin{array}{l}O-C\cdot CO_2H\\ CO\cdot CH\end{array}$, which crystallises from glacial acetic acid in white needles, and melts at 277—278° forming *α-naphthachromone*,  $C_{10}H_6<\begin{array}{l}O-CH\\ CO\cdot CH\end{array}$. This separates from dilute alcohol in lustrous, efflorescent, white needles, and is hydrolysed by alcoholic sodium ethoxide to 2-acetyl-α-naphthol and formic acid. W. A. D.

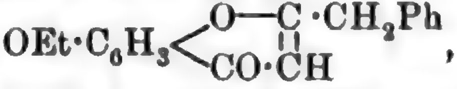
5 : 7-Dihydroxychromone. By Stanislaus von Kostanecki and J. C. de Ruijter de Wildt (*Ber.*, 1902, **35**, 861—865).—Ethyl 2-hydroxy-4 : 6-dimethoxybenzoylpyruvate,

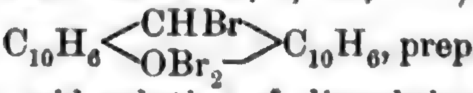
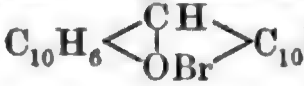
$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et,$$

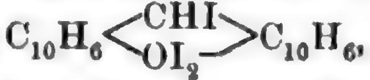
obtained by condensing phloracetophenone dimethyl ether with ethyl oxalate by means of sodium, crystallises from alcohol in yellowish, rhombic plates, melts at 149°, and is converted by boiling hydrochloric acid of sp. gr. 1·19 into 5 : 7-*dimethoxychromone-2-carboxylic acid*,  $C_6H_2(OMe)_2<\begin{array}{l}O-C\cdot CO_2H\\ CO\cdot CH\end{array}$, which separates from alcohol in colourless needles containing $1H_2O$; the anhydrous substance melts at 244·5° and is transformed thereby with loss of carbon dioxide into 5 : 7-*dimethoxychromone*,  $C_6H_2(OMe)_2<\begin{array}{l}O-CH\\ CO\cdot CH\end{array}$. This crystallises from water in white needles containing $1H_2O$, melts, when dry, at 131—132°, and, by boiling hydriodic acid, is converted into 5 : 7-*dihydroxychromone*, which crystallises from alcohol in white plates and melts at 273°; the latter, on being boiled with a methyl alcoholic solution of methyl iodide and potassium hydroxide, yields 5-*hydroxy*-7-*methoxychromone*, which crystallises from alcohol in needles and melts at 117—118°; the hydroxyl group in position 5 is protected by the adjacent carbonyl radicle, but on boiling the ether with acetic anhydride containing sodium acetate, it yields 5-*acetoxy*-7-*methoxychromone*, which crystallises from dilute alcohol in long, lustrous needles and melts at 141°.

[With H. Feinstein].—*Ethyl* 2-*hydroxy*-4-*methoxybenzoylpyruvate*,

$OMe\cdot C_6H_3(OH)\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et$, prepared from resacetophenone monomethyl ether and ethyl oxalate, crystallises from alcohol, melts at 107—108°, and with boiling hydrochloric acid yields 7-*methoxychromone-2-carboxylic acid*,  $OMe\cdot C_6H_3<\begin{matrix}O\text{—}C\cdot CO_2H \\ \| \\ CO\cdot CH\end{matrix}$; this crystallises from alcohol in needles and melts at 261°, being thereby converted into 7-*methoxychromone*, melting at 110°. W. A. D.

Synthesis of 7-Hydroxy-2-benzylchromone. By O. Hannach and Stanislaus von Kostanecki (*Ber.*, 1902, **35**, 866—868).—ω-*Phenacetyl*-2 : 4-*diethoxyacetophenone*, $C_6H_3(OEt)_2\cdot CO\cdot CH_2\cdot CO\cdot CH_2Ph$, obtained by condensing resacetophenone diethyl ether with ethyl phenylacetate by means of sodium, crystallises from dilute alcohol in white leaflets, melts at 75°, and by boiling hydriodic acid of sp. gr. 1·96 is converted into 7-*ethoxy-2-benzylchromone*,  $OEt\cdot C_6H_3<\begin{matrix}O\text{—}C\cdot CH_2Ph \\ \| \\ CO\cdot CH\end{matrix}$, which separates from alcohol in long, white needles, melts at 154°, and is hydrolysed by alcoholic sodium ethoxide into resacetophenone monoethyl ether and phenylacetic acid. 7-*Hydroxy-2-benzylchromone*, crystallises from alcohol in white prisms and melts at 183°; 7-*acetoxy-2 benzylchromone* resembles it and melts at 114°. W. A. D.

Dibromodinaphthaxanthonium Bromide and Di-iododinaphthaxanthonium Iodide and the Bromohydrin-dibromide and the Iodohydrin-di-iodide of the so-called Dinaphthylene Glycol. By Robert Fosse (*Compt. rend.*, 1902, **134**, 177—179. Compare Abstr., 1901, i, 322, 384, 604, 643, and this vol., i, 51, 171).—*Dibromodinaphthaxanthonium bromide*,  $C_{10}H_6<\begin{matrix}CHBr \\ OBr_2\end{matrix}>C_{10}H_6$, prepared by adding bromine to a glacial acetic acid solution of dinaphthaxanthonium bromide,  $C_{10}H_6<\begin{matrix}CH \\ | \\ OBr\end{matrix}>C_{10}H_6$, is also obtained by adding bromine to dinaphthaxanthen or to the bromohydrin of the so-called dinaphthylene glycol; it regenerates dinaphthaxanthen when boiled with alcohol, acetaldehyde and hydrogen bromide being simultaneously produced.

Di-iododinaphthaxanthonium iodide,  $C_{10}H_6<\begin{matrix}CHI \\ OI_2\end{matrix}>C_{10}H_6$, obtained by adding iodine to a benzene solution of dinaphthaxanthen, crystallises in red needles; it may also be formed from the so-called naphthylene glycol. G. T. M.

Hydrazides and Azoimides of Organic Acids. XXV. Hydrazide [and Azoimide] of α-Thiophencarboxylic Acid. By Theodor Curtius and Heinrich Thyssen (*J. pr. Chem.*, 1902, [ii], **65**, 1—19). —α-*Thiophencarboxylic hydrazide*, $C_4SH_3\cdot CO\cdot N_2H_3$, prepared by long boiling of ethyl α-thiophencarboxylate with hydrazine hydrate, crystallises in long needles, melts at 136° and exhibits the usual properties of the hydrazides; the *hydrochloride* forms small, white needles melting and decomposing at 247°. The *sodium* derivative of the hydrazide is a yellow precipitate.

Benzylidene-a-thiophencarboxylic hydrazide, $C_4SH_3{\cdot}CO{\cdot}N_2H{:}CHPh$, prepared from the hydrazide and benzaldehyde, crystallises in lustrous needles melting at 177°. *o-Hydroxybenzylidene-a-thiophencarboxylic hydrazide*, $C_4SH_3{\cdot}CO{\cdot}N_2H{:}CH{\cdot}C_6H_4(OH)$, crystallises in yellow needles melting at 176°; the *compound* obtained from ethyl acetoacetate and the hydrazide, $C_4SH_3{\cdot}CO{\cdot}N_2H{:}CMe{\cdot}CH_2{\cdot}CO_2Et$, forms crystals melting at 112°; *β-propylidene-a-thiophencarboxylic hydrazide*,

$$C_4SH_3{\cdot}CO{\cdot}N_2H{:}CMe_2,$$

prepared from acetone and the hydrazide, forms crystals melting at 108°; *a-thiophencarboxylic acetylhydrazide*, $C_4SH_3{\cdot}CO{\cdot}N_2H_2{\cdot}COMe$, forms crystals melting at 172°; *a-thiophencarboxylic benzoylhydrazide*, $C_4SH_3{\cdot}CO{\cdot}N_2H_2{\cdot}COPh$, is prepared by the Schotten-Baumann method. *s-Dithiophencarboxylic hydrazide*, $N_2H_2(CO{\cdot}C_4SH_3)_2$, prepared by the action of iodine on an alcoholic solution of the hydrazide, forms crystals melting at 262°.

a-Thiophencarboxylic azoimide, $C_4SH_3{\cdot}CO{\cdot}N_3$, prepared by careful addition of sulphuric acid to a solution containing the hydrazide and sodium nitrite, forms a yellow, crystalline mass melting at 37°.

a-Thiophencarboxylic anilide, $C_4SH_3{\cdot}CO{\cdot}NHPh$, prepared from the azoimide and aniline, crystallises in leaflets melting at 140° and is identical with the substance prepared from phenylcarbimide, thiophen and aluminium chloride (Leuckart and Schmidt, Abstr., 1885, 1224).

s-Phenyl-a-thiophencarbamide, $NHPh{\cdot}CO{\cdot}NH{\cdot}C_4SH_3$, prepared by heating the azoimide with aniline, crystallises in needles melting and decomposing at 215°. *a-Thiophenurethane*, $C_4SH_3{\cdot}NH{\cdot}CO_2Et$, prepared by boiling the azoimide with absolute alcohol, crystallises in lustrous, colourless needles melting at 48°. *s-Di-a-thiophencarbamide*, $CO(NH{\cdot}C_4SH_3)_2$, prepared by warming the azoimide with water, crystallises in brownish or greyish-violet needles melting at 224°. All attempts to prepare *a*-thiophenamine from the urethane failed.

K. J. P. O.

Oxidation of *a-iso*Cinchonine. By Zdenko H. Skraup and R. Zwerger (*Monatsh.*, 1901, **22**, 1083—1096. Compare Abstr., 1900, i, 605).—*a-iso*Cinchonine, when treated with methyl iodide, yields a stable *methiodide* melting at 252—253°. By treatment of *a-iso*cinchonine hydriodide with methyl iodide, the hydriodide of an isomeric methiodide, melting at 247—248°, is obtained. This methiodide decomposes, however, when attempts are made to liberate it from its salt.

When oxidised with chromic acid, *a-iso*cinchonine yields carbon dioxide and formic, acetic, and cinchonic acids. No substance analogous to meroquinenine could be isolated. Small quantities of two products, $C_{10}H_{15}O_5N$, perhaps a hydroxypiperidinebutyric acid, and $C_6H_{16}O_5NCl$, which might be a chloropiperidinecarboxylic acid containing $3H_2O$, were isolated in the form of the platinichlorides. The formation of cinchonic acid shows that the quinoline nucleus of cinchonine is present in the same form in *a-iso*cinchonine. G. Y.

Physical Properties of *a*- and *β-iso*Cinchonine. By Zdenko H. Skraup (*Monatsh.*, 1901, **22**, 1097—1102. See Abstr., 1900, i, 606).—*a*- and *β-iso*Cinchonine are best purified by crystallisation from petroleum of low boiling point and have then practically identical melting points; *a-iso*cinchonine melted at 126—126·5°, *β-iso*cinchonine at 126—127°. The bases are heteromorphic and pseudorhombic. *a-iso*Cinchonine was found to have $[a]_D$ +49·54°; +49·74°; +51·77°; +51·85°. *β-iso*-Cinchonine at similar concentrations had $[a]_D$ −62·14°; −57·85°; −58·26°; −59·81°. The bases are therefore not enantiomorphous forms. G. Y.

Cinchonifine, Cinchotine, and Cinchonine. By ZDENKO H. SKRAUP (*Monatsh.*, 1901, **22**, 1103—1104).—The facts contained in Jungfleisch and Léger's papers (Abstr., 1901, i, 287, 338) have previously been published by other authors. G. Y.

Decomposition of Cocaine Hydrochloride in Alcoholic Solution by Hydrogen Chloride. By PAUL HORST (*Chem. Zeit.*, 1902, **26**, 27—28).—As the result of several experiments, the author concludes that the formation of methyl benzoate in the decomposition of cocaine by mineral acids or alcoholic potash is due to secondary reactions, methyl alcohol being split off from the cocaine and combining with the benzoic acid which also results from the hydrolysis. A. F.

Ecgonine. By OSWALD HESSE (*J. pr. Chem.*, 1902, [ii], **65**, 91—95).—It has been stated by Gintl and Storch (*Monatsh.*, 1887, **8**, 79) that when ecgonine is heated with methyl iodide and methyl alcohol at 100°, an additive compound, $C_9H_{15}O_3N,MeI$, is formed. The author is, however, of opinion that the platinichloride, which they described, resembled rather that of ecgonine itself than that of the additive compound.

If ecgonine is heated with methyl iodide and methyl alcohol under a reflux condenser, ecgonine methiodide, $C_9H_{15}O_3N,MeI,H_2O$, is obtained, which crystallises in colourless prisms, melts at 218°, and is easily soluble in water and fairly so in alcohol; when it is heated with hydriodic acid according to Zeisel's method, methyl iodide is not produced. The *methochloride* crystallises in large, colourless tablets containing $1H_2O$; the *aurichloride* crystallises with $1H_2O$, which it loses at 90°, and melts at 130°; the *platinichloride* also crystallises with $1H_2O$ and melts at 194°. The *hydroxide* crystallises in colourless prisms with $1H_2O$, dissolves readily in water, and has $[a]_D$ −42·4°; by the action of benzoyl chloride on it, benzoylecgonine *methochloride* is obtained, which crystallises in colourless plates.

Ecgonine ethiodide crystallises in colourless prisms containing $2H_2O$; when slowly heated, it loses its water of crystallisation at 160° and melts at 192°, but if heated rapidly it melts at about 185°. The *hydroxide* forms long, colourless prisms containing $1H_2O$, which is eliminated at 120°; it melts and decomposes at 202°; its aqueous solution is of neutral reaction. E. G.

Corydalis Alkaloids. By JOHANNES GADAMER, with H. ZIEGENBEIN and H. WAGNER (*Arch. Pharm.*, 1902, **240**, 19—52. Compare Abstr., 1901, i, 288; Trans., 1894, **65**, 25; 1901, **79**, 87).—By an improved method of extraction, more than 400 grams of alkaloids, including some new ones, have been obtained from 10 kilos. of the tubers of *Corydalis cava*. There were obtained: (i) in ethereal solution; A, crystalline bases which were separated by fractional extraction with alcohol, whereby corydaline, bulbocapnine, corycavine and corybulbine were obtained in this order; B, an amorphous mixture of bases, which were converted into hydrobromides and precipitated fractionally with ammonia, when there were obtained in the following order, beginning with the weakest base, *a* (crystalline), corydaline, corybulbine, iso*corybulbine*, *corycavamine*, corycavine, *corydine*, bulbocapnine, and a base melting at 135° of unknown strength; *b* (amorphous), 1, a base of medium strength, forming a crystalline hydrochloride; 2, a mixture of amorphous bases forming amorphous salts. (ii) Insoluble in ether, precipitated by chloroform from the strong ammoniacal aqueous solution, corytuberine. Protopine was not detected.

The crystalline bases fall into three groups. 1, Corydaline, corybulbine and *iso*corybulbine; weak bases, oxidised by alcoholic iodine solution to compounds resembling berberine. 2, Corycavine and corycavamine; bases of medium strength, attacked by iodine solutions. 3. Bulbocapnine, corydine, and corytuberine; strong bases, oxidised by iodine solution but yielding no well characterised products (probably owing to the presence of the free hydroxyl group).

The action of these alkaloids on an alcoholic iodine solution (the digestion was continued for 3 hours at 100°) cannot be used for purposes of quantitative estimation. Under these circumstances, the iodine attacks the alcohol to some extent; and, although the addition of hydriodic acid retards this action, it also retards the action on the alkaloid.

When corydaline is dissolved in strong sulphuric acid and the solution allowed to remain for a day at the ordinary temperature, *corydalinesulphonic acid*, $C_{22}H_{26}O_4N\cdot SO_3H$, is formed. This melts above 260°, is insoluble in water, and forms an amorphous *potassium* salt.

When corydaline is oxidised with alcoholic iodine and the product reduced with zinc and dilute sulphuric acid, optically inactive corydaline is obtained; most of it melts at 134—135°, but occasionally some melted at 156—157°. The first variety could not be separated into active components, and therefore is probably *i*-corydaline, inactive by internal compensation. By crystallising the bromocamphorsulphonate of the second variety from water, a partial separation was effected, the alkaloid regenerated from the crystals being dextrorotatory in chloroform solution; this variety may, therefore, be regarded as the racemic form, *r*-corydaline.

iso*Corybulbine*, $C_{21}H_{25}O_4N$ or $C_{18}H_{16}ON(OMe)_3$, melts at 179—180° and is very sensitive to light. C. F. B.

Laudanine. By Oswald Hesse (*J. pr. Chem.*, 1902, [ii], 65, 42—45. Compare Abstr., 1895, i, 110).—The author has previously suggested (*loc. cit.*) that laudanosine is the methyl ether of laudanine; the latter contains three methoxy-groups and one hydroxyl, and forms a *sodium* salt, $C_{20}H_{24}O_4NNa,4H_2O$, which crystallises in small, white prisms. On treating the alkaloid or the sodium salt with methyl iodide in cold methyl alcohol, a small amount of *r*-laudanosine is obtained, which forms white crystals insoluble in alkalis. With ethyl iodide, 80 per cent. of an *ethyl* ether of laudanine, $C_{20}H_{24}O_4NEt$, is obtained as an amorphous mass, which melts at 40—50°, is alkaline in reaction, and gives no colour reaction with ferric chloride. The *hydrochloride* crystallises, with $5H_2O$, in colourless prisms; the platinichloride, with $2H_2O$, is a yellow, crystalline precipitate. K. J. P. O.

New Derivatives of Bismuth Chloride and Iodide. By Ludwig Vanino and Otto Hauser (*Ber.*, 1902, **35**, 663—666. Compare Abstr., 1901, i, 289).—*Bismuth iodide pyridine hydrochloride*, BiI_3,C_5NH_5,HCl, obtained by dissolving bismuth pyridine iodide in dilute hydrochloric acid, crystallises in ruby-red prisms. The *salt*, $2BiI_3,3C_5NH_5,HI$, obtained by dissolving the compound $2BiCl_3,3C_5NH_5$ in an excess of hydriodic acid of sp. gr. 1·7, forms red crystals and is not affected by hydrogen chloride; the quinoline *salt*, BiI_3,C_9NH_7,HI, obtained similarly from bismuth quinoline chloride, closely resembles the pyridine compound, but is decomposed by hydrogen chloride and dissolves in hydrobromic acid, giving the *compound* BiI_3,C_9NH_7,HBr; this forms bright orange, silky crystals.

Bismuth diethylaniline chloride, $BiCl_3,2NEt_2Ph,HCl$, forms large, white crystals, and *bismuth dimethylaniline chloride*,

$$BiCl_3,2NMe_2Ph,HCl,$$

small prisms; the *salt*, $BiCl_3,3NEt_2Ph,HCl$, also crystallises well. These compounds are not hygroscopic and are only slowly decomposed by water. W. A. D.

Some Compounds of Pyridine with Cupric and Cuprous Thiocyanates. By Franz M. Litterscheid (*Arch. Pharm.*, 1902, **240**, 74—77. Compare Abstr., 1901, i, 635).—When freshly precipitated cupric thiocyanate is dissolved in boiling pyridine and the solution allowed to cool, lustrous, green crystals of a compound, $Cu(C_5NH_5{\cdot}CNS)_2,2C_5NH_5$, separate. These lose pyridine when warmed with water or kept in the air, forming the compound $Cu(C_5NH_5{\cdot}CNS)_2$, which is coloured a brighter green.

When cupric thiocyanate is dissolved in excess of pyridine and sulphur dioxide is passed into the hot solution, a colourless compound, $Cu_2(C_5NH_5{\cdot}CNS)_2,C_5NH_5$, separates; this readily loses pyridine, forming a compound, $Cu_2(C_5NH_5{\cdot}CNS)_2$, which can also be obtained by treating freshly precipitated cuprous thiocyanate with pyridine; this compound is decomposed when boiled with pyridine, the cupric compound being formed.

Cuprosocupric thiocyanate does not form a compound with pyridine; a mixture of cupric and cuprous compounds is obtained instead.

C. F. B.

Action of Acetyl Chloride, Benzoyl Chloride, and Ethylidenelactic Acid on Pyridinecholine. By [Ernst Schmidt and] Franz M. Litterscheid (*Arch. Pharm.*, 1902, **240**, 77—80. Compare Nothnagel, Abstr., 1894, i, 437).—When pyridinecholine chloride

(Roithner, Abstr., 1895, i, 319) is heated with acetyl chloride for 3 hours, it is partly converted into *acetylpyridinecholine chloride*, $C_5NH_5Cl\cdot CH_2\cdot CH_2\cdot OAc$, of which the *platinichloride* and *aurichloride* melt at 193—194° and 143—144° respectively. When boiled for 2 hours with benzoyl chloride, it is converted entirely into *benzoylpyridinecholine* chloride, $C_5NH_5Cl\cdot CH_2\cdot CH_2\cdot OBz$, the *platinichloride* and *aurichloride* of which melt at 201° and 128—129° respectively. With lactic acid, it will not combine. C. F. B.

The Carbon Double Linking and the Carbonyl Radicle. By Daniel Vorländer (*Annalen*, 1902, **320**, 66—98).—Radicles, when attached to carbonyl, acquire properties differing considerably from those which they possess in other states of combination. The hydroxyl and chlorine radicles of the organic acids and their chlorides have properties which are not manifested by these radicles when combined with alkyl groups. If this alteration in the properties of a group attached to carbonyl is general, then the carbon residue of the double linking in an α-unsaturated compound should vary in its reactivity according as to whether it is attached to carbonyl or not. The hydroxyl radicle when united with carbonyl, is distinguished from the group in other combinations by a marked increase in the electrochemical difference between its oxygen and hydrogen atoms; a similar, but less appreciable, difference is noticed between the electrical condition of the two carbon atoms of the double linking contiguous to carbonyl, the state of the two configurations being typified by the formulæ $\overset{+}{H}\overset{-}{O}\cdot C\colon O$ and $\overset{+}{C}\colon\overset{-}{C}\cdot C\colon O$ respectively. Accordingly, the addition of the compound $\overset{+}{H}\overset{-}{R}$ leads to the formation of the additive product $CR\cdot CH\cdot C\colon O$, and not to that of the isomeride $CH\cdot CR\cdot C\colon O$.

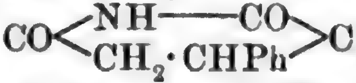
The interpolation of a methylene residue between the carbonyl group and the substituent radicle or double linking completely annuls this variation in electrical condition, and a substance containing the residue $HO\cdot CH_2\cdot CO$ behaves like an ordinary alcohol, whilst the double linking in the configuration $C\colon C\cdot CH_2\cdot CO$ is destitute of the reactivity which it possesses in the α-ketones.

The reactivity of the αβ-double linking in ethyl cinnamylidenemalonate, $CHPh\colon CH\cdot CH\colon CH(CO_2Et)_2$, towards hydrogen cyanide follows from the preceding generalisations, but there is also some evidence indicating that the γδ-double linking also reacts with this reagent, for a fully saturated tricarboxylic acid was obtained as the ultimate product of hydrolysis (Thiele and Meisenheimer, Abstr., 1899, i, 603).

These considerations justify the belief that the reactivity of the double linking of α-unsaturated ketones and esters is due to that property of carbonyl which brings about the increased mobility of the hydroxyl and chlorine radicles of the organic acids and their chlorides. This view is opposed to Thiele's theory of partial valency as applied to the explanation of these changes; for, according to this hypothesis, it is the ends of the system $C\colon C\cdot C\colon O$ which are reactive, so that with the reagent HR, the primary additive product is $CR\cdot C\colon C\cdot OH$, this enolic substance subsequently changing into its ketonic form. The results set forth in the experimental portion of the communication indicate that the increased activity of the double linking is not due to the negative character of the carbonyl group, for the reactivity of the amides $CHPh{:}CH\cdot CO\cdot NHR$ and $CHPh{:}CH\cdot CO\cdot NR_2$ towards ethyl sodiomalonate is even greater than that of the esters

$$CHPh{:}CH\cdot CO\cdot OR,$$

and moreover there is no apparent connection between the reactivity of the amide and the strength of the corresponding amine, the amount of interaction occurring with the piperidide being scarcely greater than that noticed in the case of the diphenylamide, in spite of the enormous difference between the strengths of piperidine and diphenylamine.

[With P. HERRMANN.]—A solution of ethyl sodiomalonate in ethyl alcohol is employed as the reagent for testing the reactivity of the double linking. Additive products were not obtained with the following unsaturated compounds: styrene, stilbene, nitrophenylethylene, diphenylbutadiene, pyrrole, N-phenylpyrrole, benzylidenequinaldine, cinnamylidenephenylhydrazine, and benzylideneacetone phenylhydrazone; these substances are alike in not containing a carbonyl group. Cinnamide readily reacts with ethyl sodiomalonate, yielding the *compound*  $CO{<}\substack{NH-\!\!-CO\\ CH_2\cdot CHPh}{>}CH\cdot CO_2Et$, which crystallises from water in needles and melts at 119°; this product, when hydrolysed with hydrochloric acid, yields β-phenylglutaric acid.

Ethyl cinnamate reacts in a similar manner, but the additive compound is unstable, and is readily hydrolysed to β-phenylglutaric acid; this product being characterised by means of its *methyl* ester, which crystallises in white needles melting at 86—87°, and its anhydride, which boils at 217—219° under 15 mm. pressure and melts at 105°; the mean electrical conductivity of the acid is 0·00772.

β-Phenylglutarimide, $CHPh{<}\substack{CH_2\cdot CO\\ CH_2\cdot CO}{>}NH$, formed by heating the acid in a stream of ammonia gas, crystallises in leaflets and melts at 173—174°; *β-phenylglutaranilic acid*,

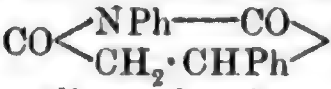
$$NHPh\cdot CO\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO_2H,$$

produced by mixing the anhydride with aniline, crystallises from alcohol in white needles and melts at 171°. The methylamide, dimethylamide, ethylamide, and diethylamide of cinnamic acid all react with ethyl sodiomalonate, the additive products were not isolated, however, but hydrolysed to β-phenylglutaric acid; the reactions were never complete, and the weight of unaltered amide was estimated in each experiment.

The diethylamide and piperidide of αβ dibromo-β-phenylpropionic acid, prepared by adding bromine to the corresponding amide and piperidide, crystallise respectively in prisms melting at 127° and in needles decomposing at 189°.

The *acid*, $C_5NH_{10}\cdot CO\cdot CH_2\cdot CHPh\cdot CH(CO_2H)_2$, results from the interaction of the piperidide of cinnamic acid and ethyl sodiomalonate after treating the mixture with mineral acid; it crystallises from ethyl acetate or water in white prisms melting at 146° with evolution of carbon dioxide; the fused product then consists of the *semipiperidide*, $C_5NH_{10}\cdot CO\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO_2H$, of β-phenylglutaric acid, and a substance which yields this acid on hydrolysis with hot hydrochloric acid.

The diphenylamide of cinnamic acid reacts with ethyl sodiomalonate, and the additive compound on hydrolysis ultimately yields β-phenylglutaric acid.

Cinnamanilide, when treated with ethyl sodiomalonate, gives rise to the *ester*  $\mathrm{CO}\left<\begin{matrix}\mathrm{NPh}\text{——}\mathrm{CO}\\ \mathrm{CH_2\cdot CHPh}\end{matrix}\right>\mathrm{CH\cdot CO_2Et}$, which crystallises from alcohol in white needles and melts at 166°, and also to the *sodium* salt of the *acid* $\mathrm{NHPh\cdot CO\cdot CH\cdot CHPh\cdot CH(CO_2Et)\cdot CO_2H}$; both these substances, when hydrolysed with cold alcoholic potassium hydroxide solution, yield the *dicarboxylic* acid, $\mathrm{NHPh\cdot CO\cdot CH_2\cdot CHPh\cdot CH(CO_2H)_2}$, this substance, when heated, furnishing phenylglutaranilic acid. Both the products of the preceding reaction, when hydrolysed with boiling hydrochloric acid, yield β-phenylglutaric acid.

Cinnamonitrile and ethyl sodiomalonate interact, the product being a viscid oil having probably the constitution

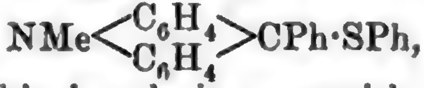
$$\mathrm{CN\cdot CH_2\cdot CHPh\cdot CH(CO_2Et)_2},$$

which, on hydrolysis with hydrochloric acid, ultimately gives rise to β-phenylglutaric acid. G. T. M.

5-Chloro- and 5-Bromo-acridine. KALLE & Co. (D.R.-P. 122607).—5 Chloroacridine, already obtained by Graebe and Lagodzinski from acridone and phosphorus pentachloride (Abstr., 1893, i, 649), is prepared by heating thioacridone with phosphorus pentachloride and phosphorus oxychloride at 120—125°.

5-*Bromoacridine*, $\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{CBr}\\ |\\ \mathrm{N}\text{—}\end{matrix}\right>\mathrm{C_6H_4}$, produced by treating thioacridone with red phosphorus and bromine, and extracting the product with 30—40 per cent. sulphuric acid, melts at 116—117; it is accompanied by another basic substance melting at 255°, which is insoluble in ether. G. T. M.

ψ-Ammonium Bases and their Derivatives. By ARTHUR HANTZSCH and ARTHUR HORN (*Ber.*, 1902, **35**, 877—883).—The reversion of ammonium hydroxide bases to alcoholic ψ-bases and of their salt-likecyanides to the organic cyanides of the ψ-bases in the acridinium series (Hantzsch and Kalb, Abstr., 1899, i, 400; 1900, i, 113) is paralleled by the behaviour of the thiols $\vdots\mathrm{NMe\cdot SH}$ and their ethers $\vdots\mathrm{NMe\cdot SPh}$, which immediately revert to derivatives of the ψ-base.

5-*Phenyl*-10-*methylthioacridol*, $\mathrm{NMe}\left<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{CPh\cdot SH}$, prepared from phenylmethylacridinium chloride and sodium hydrogen sulphide, is a yellowish-white substance which melts at 105—109°, is insoluble in water, slightly soluble in alcohol, and readily so in benzene and carbon disulphide, thus resembling the mercaptans rather than the metallic sulphides; it is readily decomposed into hydrogen sulphide and phenylmethylacridol. The *phenyl ether*,  $\mathrm{NMe}\left<\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{CPh\cdot SPh}$, from the acridinium chloride and sodium thiophenol, is a greyish-yellow substance, soluble in alcohol, benzene, or chloroform, and is readily hydrolysed to thiophenol and phenylmethylacridol.

On the other hand, phenylmethylacridinium chloride and acridol both give, with sodium toluenesulphinate, a true *sulphinate*,

$\mathrm{CPh}\left<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}\right>\mathrm{NMe}\cdot SO_2\cdot C_7H_7$, which forms golden-yellow spangles, melts at 208°, and dissolves readily in water and alcohol, but not in benzene, ether, or chloroform; the isomeric sulphone of the ψ-base could not be prepared. T. M. L.

Action of Aluminium Chloride on Phenylenediamine Nitrate.

By Emilio Gabutti (*L'Orosi*, 1901, **24**, 366—368).—m-*Phenylenediamine nitrate*, $C_6H_4(NH_2)_2,2HNO_3$, forms large, shining crystals, readily soluble in water or alcohol. When heated with aluminium chloride, it yields a m-*phenylenenitrodiamine*, $C_6H_4(NH\cdot NO_2)_2$, which is obtained as a pale yellow oil with a characteristic odour and a strong acid reaction; it boils and violently explodes at 90°, and is soluble in ether. T. H. P.

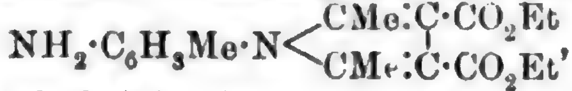
Relative Basicity of the two Amino-groups in Substituted Diamines. III. *p*-Tolylenediamine $[CH_3 : NH_2 : NH_2 = 1 : 2 : 5]$.

By Carl Bülow and Georg List (*Ber.*, 1902, **35**, 681—688).—*Ethyl* p-*tolylene-bis-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate*,

$$C_6H_3Me\left(N<\begin{matrix}CMe{:}C\cdot CO_2Et\\ \vert\\ CMe{:}C\cdot CO_2Et\end{matrix}\right)_2,$$

prepared by the interaction of *p*-tolylenediamine hydrochloride and ethyl diacetylsuccinate, crystallises from dilute alcohol in minute scales, melts at 134°, and gives the pyrrole reaction with a pine-splinter. The *acid*, $C_{23}H_{22}O_8N_2$, crystallises from dilute alcohol and melts at 275° with liberation of carbon dioxide. The acid *silver* salt, $C_{23}H_{20}O_8N_2Ag_2$, is a reddish-white powder.

Ethyl 1-m-*amino-o-tolyl-2 : 5-dimethylpyrrole-3 : 4 dicarboxylate*,



$$NH_2\cdot C_6H_3Me\cdot N<\begin{matrix}CMe{:}C\cdot CO_2Et\\ \vert\\ CMe{:}C\cdot CO_2Et\end{matrix}$$

crystallises from alcohol in long, slender, grey needles, melts at 105—106°, and shows the pine-splinter reaction; the free amino-group can be diazotised and the product condensed to an azo-dye with β-naphthol-3 : 6-disulphonic acid. In order to determine with which amino-group condensation had taken place, the compound was diazotised and the product identified with that from *o*-toluidine and ethyl diacetylsuccinate; 1-o-*tolyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid*, $C_{15}H_{15}O_4N$, crystallises from alcohol in reddish, prismatic forms, melts at 203—204° with liberation of carbon dioxide, and shows the pine-splinter reaction; the acid *silver* salt was prepared and analysed.

1-m-*Tolyl-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid*, from *m*-toluidine and ethyl diacetylsuccinate, melts and decomposes at 222—223°; the acid *silver* salt was analysed.

1-m-*Tolyl-2 : 5 dimethylpyrrole*, prepared by distilling the preceding acid under slightly reduced pressure, crystallises from ether, melts at 53°, and is volatile in a current of steam. T. M. L.

Nitro- and Amino-derivatives of the Xylenes. By EMILIO NOELTING and G. THESMAR (*Ber.*, 1902, **35**, 628—650. Compare Abstr., 1901, i, 588).—4 : 6-*Dinitro-2-acetylamino*-m-*xylene*, obtained by nitrating at 0° acetyl-2-*m*-xylidide dissolved in concentrated sulphuric acid, crystallises in white needles, melts and decomposes at 226—228°, and on hydrolysis with concentrated hydrochloric acid yields 4 : 6-*dinitro-2-amino*-m-*xylene*; this crystallises from alcohol in small, yellow leaflets, melts at 174—175°, and is reduced by ammonium sulphide to 6-*nitro*-2 : 4-*diamino*-m-*xylene*, which separates from boiling water in long, slender, orange-coloured needles and melts at 151—152°.

The nitration of 4-nitro-*o*-xylene dissolved in concentrated sulphuric acid with a mixture of sulphuric and nitric acids takes place at the ordinary temperature, and is completed by warming for 10 minutes on the water-bath; the product is a mixture of 4 : 5-*dinitro*- and 4 : 6-*dinitro*-o-*xylenes*, which can be separated by fractional crystallisation from alcohol. 4 : 5-*Dinitro*-o-*xylene* is the more sparingly soluble and crystallises in slender, white needles melting at 115—116°; it differs from its congener in being easily converted by alcoholic ammonia at 150° into 5-nitro-4-amino-*o*-xylene. This fact can be utilised in isolating 4 : 6-*dinitro*-o-*xylene*, which crystallises in white needles, melts at 75—76°, is reduced by ammonium sulphide to 6-nitro-4-amino-*o*-xylene (m. p. 74—75°) and by tin and hydrochloric acid to *o*-xylylene-*m*-diamine.

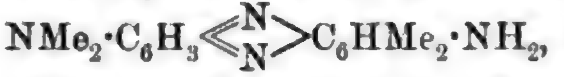
The nitration of 3-nitro-*o*-xylene yields a complex mixture, and an attempt to obtain a trinitro-*o*-xylene by energetically nitrating *o*-xylene gave only a mixture of dinitro-derivatives; Drossbach's trinitro-compound melting at 178° is really trinitro-*m*-xylene, derived from *m*-xylene present as an impurity.

A table is given differentiating the eleven xylylenediamines by their behaviour with ferric chloride, potassium dichromate, sodium nitrite, and bleaching powder; the diamines are best obtained by the reduction of the corresponding nitroxylidines with zinc dust in neutral solution according to Bamberger's method, and when pure do not become coloured on keeping. 3 : 4-*Diacetylamino*-o-*xylene* crystallises from benzene in small, white needles, and melts at 196—197°; 4 : 5-, 3 : 5-, and 3 : 6-*diacetylamino*-o-*xylenes* are similar, and melt respectively at 227—228°, 240—241°, and 275—276°. 2 : 5-*Diamino*-m-*xylene*, obtained by reducing the azo-compound from 2-*m*-xylidine and diazobenzene-*m*-sulphonic acid, crystallises from a mixture of benzene and light petroleum in nacreous leaflets and melts at 103—104°.

The following azines were prepared from the *o*-diamines by means of phenanthraquinone. 1 : 2-*Xylophenanthrazine* forms small, yellow needles melting at 223—224°; 2 : 3-*xylophenanthrazine*, brownish-yellow leaflets melting at 291—292°; 1 : 3- and 1 : 4-*xylophenanthrazine*, flat, yellowish needles melting at 206—207° and 285—286° respectively.

s-Xylylene-*o*-diamine interacts in dilute aqueous acetic acid solution with bleaching powder at 0°, giving 1 : 2-*xylo*-4 : 5-*quinonedichlorodiimide*, $C_6H_2Me_2(NCl)_2$, which crystallises from ether in long, bright yellow needles, darkens at 70°, and explodes at 87°; it decomposes rapidly at the ordinary temperature, becoming black in 24 hours. Attempts to obtain similar quinoneimides from other xylylene-*o*-diamines gave yellow powders which, although more stable, could not be crystallised and had no definite composition.

The following chrysoidines were prepared from the corresponding *m*-diamines. 3 : 5-*Diamino*-o-*xylene*-6-*azobenzene,* obtained from *o*-xylylene-*m*-diamine, crystallises from dilute alcohol in long, scarlet-red needles and melts at 127°; 3 : 5-*diamino*-o-*xylene*-4-*azobenzene,* which is produced simultaneously, forms bright red leaflets, melts at 171—172°, and has little tinctorial power. 4 : 6-*Diamino*-m-*xylene*-5-*azobenzene* crystallises in red leaflets, 2 : 4-*diamino*-m-*xylene*-5-*azobenzene* in scarlet needles melting at 97·5—98°, and 3 : 5-*diamino*-p-*xylene*-2-*azobenzene* in orange needles melting at 90—91°.

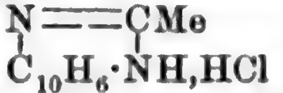
The following eurhodines were prepared by the aid of *p*-nitrosodimethylaniline hydrochloride. 3′-*Dimethylaminopheno*-3-*amino*-1 : 2-*xylazine,*  $NMe_2\cdot C_6H_3\left\langle\begin{smallmatrix}N\\N\end{smallmatrix}\right\rangle C_6HMe_2\cdot NH_2$, forms yellow needles and melts and decomposes at 265°; 3′-*dimethylaminopheno*-3-*amino*-2 : 4-*xylazine* crystallises in brownish-red needles melting at 241—242°, and 3′-*dimethylaminopheno*-3-*amino*-1 : 4-*xylazine* in small, yellow needles melting at 215—216°.

1 : 2-*Xylo*-3 : 6-*quinonedichlorodiimide* crystallises from dilute alcohol in slender, yellow needles and melts at 105·5°; 1 : 3-*xylo*-2 : 5-*quinonedichlorodiimide* is similar, melts at 112°, and decomposes at 175°; 1 : 4-*xylo*-2 : 5-*quinonedichlorodiimide* forms slender, slightly brown needles melting at 124° and decomposing at 137°.

o-, *m*-, and *p*-Xylosafranines were prepared from the corresponding *p*-diamines. W. A. D.

5 : 4′-Dichloro-2-aminodiphenylamine. By E. Wilberg (*Ber.*, 1902, **35**, 954—959).—5 : 4′-*Dichloro*-2-*aminodiphenylamine,* obtained when di-*p*-dichlorohydrazobenzene is treated with stannous chloride and hydrochloric acid, crystallises from benzene and light petroleum in small, white needles, and melts at 91°. It forms with carbon disulphide a *thiocarbamide* melting at 273°, with benzil, a *stilbazonium* compound melting at 213°, and with nitrous acid, an *azoimide* melting at 204°. The *hydrochloride* crystallises in slender, white needles and, when heated with water in a sealed tube at 200°, yields *p*-chloroaniline and 4′-*chloro*-2-*aminodiphenylamine,* which crystallises in long, white needles, melts at 119°, and forms an *azoimide* melting at 154°. 4′-Chloro-2-aminodiphenylamine can also be obtained by the reduction of 4′-*chloro*-2-*nitrodiphenylamine,* which is obtained by heating a mixture of *o*-chloronitrobenzene, *p*-chloroaniline, and sodium acetate at 170—190° for 10 hours and crystallises in long, orange-red needles melting at 145·5°. 5 : 4-Dichloro-2-aminodiphenylamine hydrochloride, when heated at 230—235° for 10 minutes, yields a *fluorindine,* $C_{36}H_{21}N_5Cl_4$, which crystallises from nitrobenzene in lustrous, bronze-green needles and forms a *dihydrochloride* which crystallises in lustrous, dark violet-red needles. R. H. P.

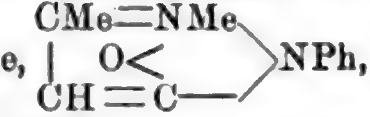
Formation of Rings from 1 : 8-Derivatives of Naphthalene. By Emilio Noelting (*Chem. Zeit.*, 1902, **26**, 5).—1 : 8-Naphthylenediamine readily yields iminoazoles. Thus, by the reduction of acetyl-1 : 8-nitronaphthylamine with stannous chloride and hydrochloric acid, the author obtained the iminoazole hydrochloride,



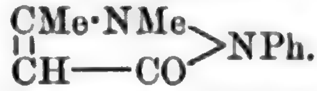
$$\begin{array}{l} N{=\!=}CMe \\ | \qquad\quad | \\ C_{10}H_6{\cdot}NH,HCl \end{array}$$

This is a yellow, crystalline salt, rather sparingly soluble in cold, but readily in hot, water. It also dissolves readily in alcohol, but is insoluble in ether or benzene. The free base is precipitated by alkali hydroxide or by an acetate, but could not be obtained crystalline. When heated with phthalic anhydride and zinc chloride, it yields a yellow colouring matter. The corresponding phenyliminoazole is obtained by the reduction of benzoyl-1 : 8-nitronaphthylamine. It dyes silk and cotton, mordanted with tannin, yellow, although no tinctorial properties are possessed by the preceding methyl compound. With dimethyl-*p*-aminobenzaldehyde and protocatechuic aldehyde, 1 : 8-naphthylenediamine yields the dimethylamino- and the dihydroxy-derivatives of Ladenburg's aldehydin. Both these compounds have tinctorial properties. A. F.

Thio- and Seleno-antipyrines and the Constitution of Antipyrine. By AUGUST MICHAELIS (*Annalen*, 1902, 320, 1—51).—The properties of antipyrine and its modes of formation are most easily explained on the assumption that it is a 2:5-pyrazole,



and not an *iso*pyrazolone of the constitution

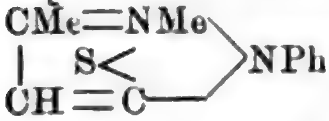


$$\begin{array}{l} CMe{\cdot}NMe \\ \| \\ CH{-\!-}CO \end{array}\!\!>\!NPh.$$

These two configurations are not very dissimilar; it is merely necessary to suppose that the oxygen atom is turned towards the interior of the ring so that it becomes influenced by the nitrogen atom in position 2. The imino-compound corresponding with 2 : 5-pyrazole formula has already been isolated (Michaelis and Gunkel, Abstr., 1901, i, 351).

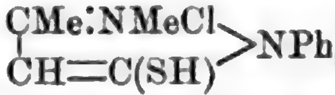
This view of the constitution of antipyrine derives considerable support from a study of the properties of its thio- and seleno-analogues.

[With H. BINDEWALD.]—Thioantipyrine (compare this vol., i, 120),



(1-phenyl-2 : 3-dimethyl-2 : 5-thiopyrazole), develops a transient, green coloration with ferric chloride, but not with nitrous acid; it is a less energetic antipyretic than antipyrine, but has no injurious after effects. Warm-blooded animals are not injured by subcutaneous and intravenous injections of the thio-compound; the nerves and mucous membrane are likewise unaffected. Thioantipyrine has a toxic action on the frog, whereas an equal dose of antipyrine is without effect.

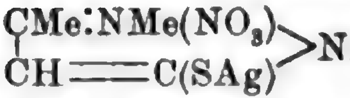
Thioantipyrine hydrochloride,



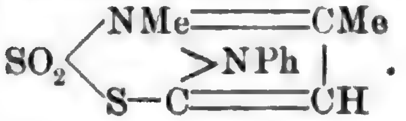
$$\begin{array}{l} CMe{:}NMeCl \\ | \\ CH{=}C(SH) \end{array}\!\!>\!NPh,$$

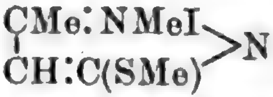
separates in colourless crystals and melts at 128°; the *platinichloride*,

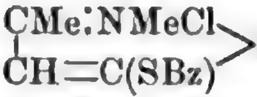
$$(C_{11}H_{12}N_2S)_2,H_2PtCl_6,2H_2O,$$

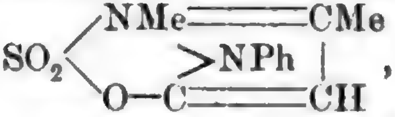
is a brownish-red precipitate melting and decomposing at 215°; the *sulphate*, $C_{11}H_{12}N_2S,H_2SO_4$, separates in colourless, cubical crystals. The silver nitrate,  $\left.\begin{array}{l}\mathrm{CMe{:}NMe(NO_3)}\\ \mathrm{CH{=}C(SAg)}\end{array}\right\rangle\mathrm{NPh}$, crystallises in long, white needles melting at 110° and containing $1H_2O$, the corresponding *mercurichloride*, $C_{11}H_{12}N_2S,HgCl_2$, is a white precipitate, the *aurichloride*, $C_{11}H_{12}N_2S,HAuCl_4$, separates as a flesh-coloured precipitate.

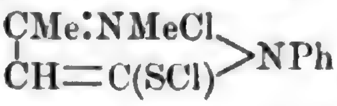
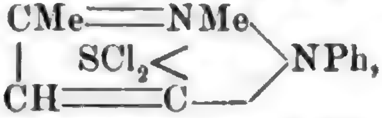
The *compound*, $C_{11}H_{12}N_2S,SO_2$, obtained as a yellow, crystalline precipitate on mixing aqueous solutions of thioantipyrine and sulphur dioxide, melts at 89—91°, and is reconverted into thioantipyrine when its alcoholic solution is evaporated; it probably has the constitution

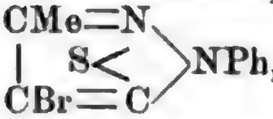


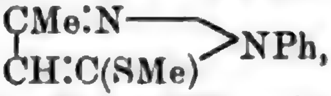
Thioantipyrine methiodide,  $\left.\begin{array}{l}\mathrm{CMe{:}NMeI}\\ \mathrm{CH{:}C(SMe)}\end{array}\right\rangle\mathrm{NPh}$, produced by mixing its generators, either alone or in alcoholic solution, crystallises from water in white needles with $1H_2O$ and melts at 90—92°; it separates from alcohol in anhydrous needles melting at 192°. When the methiodide is treated with a hot aqueous solution of sodium hydroxide, it is decomposed, yielding antipyrine, methyl mercaptan, and sodium iodide; silver oxide produces the same decomposition, but an unstable substituted ammonium hydroxide is formed as an intermediate product. *Thioantipyrine methochloride* is obtained either by neutralising the unstable hydroxide with hydrochloric acid or by treating the methiodide with silver chloride.

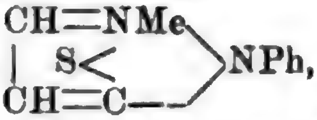
Thioantipyrine benzoyl chloride,  $\left.\begin{array}{l}\mathrm{CMe{:}NMeCl}\\ \mathrm{CH{=}C(SBz)}\end{array}\right\rangle\mathrm{NPh}$, prepared by mixing thioantipyrine and benzoyl chloride in benzene, crystallises from its chloroform solution on the addition of ether or benzene in white needles melting at 100°; it is decomposed by an aqueous solution of alkali hydroxide, yielding thioantipyrine and the corresponding alkali chloride and benzoate.

Thioantipyrine trioxide (2 *methylammonium*-1-*phenyl*-3-*methyl*-2 : 5-*pyrazolesulphonate*), , obtained by the action of oxidising agents on thioantipyrine, is readily prepared by the use of chlorine or bromine in aqueous solution; it crystallises either in white, silky needles or in well-defined, monoclinic prisms containing $1H_2O$. The hydrate loses its water at 105°, and melts indefinitely at 288—290°, evolving sulphur dioxide.

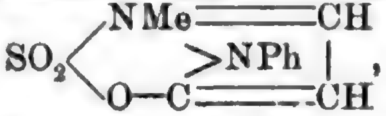
Thioantipyrine dichloride (2 : 5-*dichloro*-1-*phenyl*-2 : 3-*dimethylthiopyrazole*),  $\left.\begin{array}{l}\mathrm{CMe{:}NMeCl}\\ \mathrm{CH{=}C(SCl)}\end{array}\right\rangle\mathrm{NPh}$ or , produced by the action of dry chlorine on a chloroform solution of thioantipyrine, crystallises in unstable, yellow needles the aqueous solution of which yields on dilution a yellow oil having the composition $C_{11}H_{12}N_2SCl\cdot OH$; the latter derivative, on further decomposition with sodium hydroxide solution, furnishes thioantipyrine. The corresponding *bromide* melts at 154°, and on treatment with water yields an oily hydroxy-bromide.

Bromothioantipyrine (*4-bromo-1-phenyl-2 : 3-dimethyl-2 : 5-thiopyrazole*), , readily obtained from *5-chloro-4-bromo-1-phenyl-3-methylpyrazole methiodide*, crystallises from alcohol in prisms and from water in white needles and melts at 188° ; the methiodide itself, produced from 5-chloro-4-bromo-1-phenyl-3-methylpyrazole by the action of methyl iodide, forms white leaflets melting at 230°.

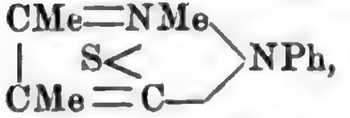
When heated, antipyrine methiodide loses methyl iodide and regenerates the original base ; thioantipyrine methiodide, on the other hand, yields *1-phenyl-3-methyl-5-thiomethylpyrazole*, , the elimination of alkyl iodide taking place at 210—220° ; the product, a colourless oil rapidly becoming yellow, boils at 196—198° under 30 mm. pressure and recombines with methyl iodide only at 100—110°, giving rise to the original methiodide.

1-*Phenyl-2-methyl*-2 : 5-*thiopyrazole*, , obtained by the action of potassium hydrosulphide on 5-*chloro*-1-*phenylpyrazole methiodide* (m. p. 172°) crystallises in needles and melts at 162° ; the *platinichloride*, $C_{10}H_{10}N_2S,H_2PtCl_6,2H_2O$, is an orange-yellow precipitate ; the *mercurichloride*, $C_{10}H_{10}N_2S,HgCl_2$, and *ferrocyanide*, $(C_{10}H_{10}N_2S)_2H_4FeCy_6$, are white, insoluble substances, the former melting at 220° ; the *methiodide* melts at 156°.

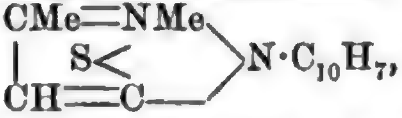
2-*Methylammonium*-1-*phenyl*-2 : 5-*pyrazolesulphonate*,



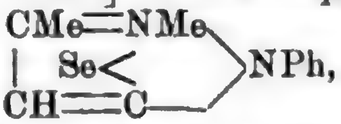
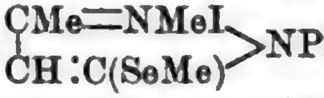
produced by the action of chlorine on an aqueous solution of 1-phenyl-2-methyl-2 : 5-thiopyrazole, separates in transparent, monoclinic crystals.

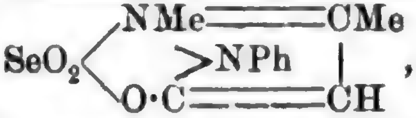
Methylthioantipyrine (1-*phenyl*-2 : 3 : 4-*trimethyl*-2 : 5-*thiopyrazole*), , prepared from 5-chloro-1-phenyl-3 : 4-dimethylpyrazole methiodide (compare Abstr., 1901, i, 407) forms white crystals melting at 129°.

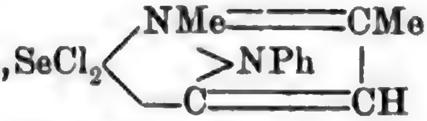
1-*β-Naphthyl*-2 : 3-*dimethyl*-2 : 5-*thiopyrazole*,

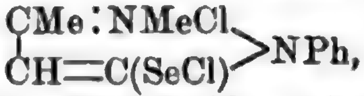


and 1-*β-naphthyl*-2 : 3 : 4-*trimethyl*-2 : 5-*thiopyrazole* melt respectively at 135° and 169°.

[With M. STEIN.]—*Selenoantipyrine* (1-*phenyl*-2 : 3-*dimethyl*-2 : 5-*selenopyrazole*), , obtained by the action of hydrogen selenide on a suspension of antipyrine in potassium hydroxide solution, separates from water, alcohol, or chloroform in lustrous, pale yellow crystals and melts at 168° ; it does not develop a coloration with ferric chloride, and only gives a faint green colour with nitrous acid. The hydrochloride and sulphate do not crystallise; the *platinichloride*, $(C_{11}H_{12}N_2Se)_2,H_2PtCl_6$, is a pulverulent, brownish-yellow precipitate; the *mercurichloride*, $C_{11}H_{12}N_2Se,HgCl_2$, and *ferrocyanide*, $(C_{11}H_{12}N_2Se)_2,H_4Fe(CN)_6$, are white, insoluble substances, the former melting at 240°. *Selenoantipyrine methiodide*,  $\begin{array}{l}\text{CMe}{=}\text{NMeI}\\ \text{CH}:\text{C(SeMe)}\end{array}\!>\text{NPh}$, obtained from its generators at the ordinary temperature, separates from water in needles and melts at 197°; the *ethiodide* melts at 152°; these alkyl iodides, when treated with potassium hydroxide solution, are decomposed, yielding antipyrine, potassium iodide, and the corresponding selenomercaptan.

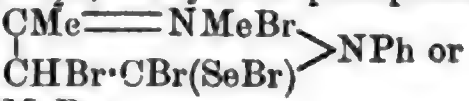
Selenoantipyrine trioxide (*2-methylammonium-1-phenyl-3-methyl-2:5-pyrazoleselenonate*),  $SeO_2\Big<\begin{array}{l}\text{NMe}{=}{=}\text{CMe}\\ \quad >\text{NPh}\quad |\\ \text{O}\cdot\text{C}{=}{=}\text{CH}\end{array}$, produced by oxidising selenoantipyrine with aqueous chlorine solution and freeing the initial product of reaction from the hydroxychloride, $C_{11}H_{12}N_2ClSe\cdot OH$, by repeated crystallisation from alcohol, separates from this solvent in needles with $1H_2O$, and decomposes at 170° with the elimination of selenium.

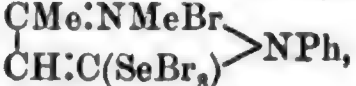
Selenoantipyrine dichloride,  $SeCl_2\Big<\begin{array}{l}\text{NMe}{=}{=}\text{CMe}\\ \quad >\text{NPh}\quad |\\ \text{—C}{=}{=}\text{CH}\end{array}$ or



$\begin{array}{l}\text{CMe}:\text{NMeCl}\\ \text{CH}{=}\text{C(SeCl)}\end{array}\!>\text{NPh}$,

prepared either by heating the trioxide with concentrated hydrochloric acid or by passing chlorine into a chloroform solution, crystallises from glacial acetic acid or alcohol in yellow needles; its *platinichloride*, $(C_{11}H_{12}N_2SeCl_2)_2PtCl_4,2H_2O$, is a yellow precipitate.

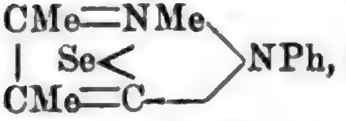
Selenoantipyrine tetrabromide,  $\begin{array}{l}\text{CMe}{=}\text{NMeBr}\\ \text{CHBr}\cdot\text{CBr(SeBr)}\end{array}\!>\text{NPh}$ or



$\begin{array}{l}\text{CMe}:\text{NMeBr}\\ \text{CH}:\text{C(SeBr}_3)\end{array}\!>\text{NPh}$,

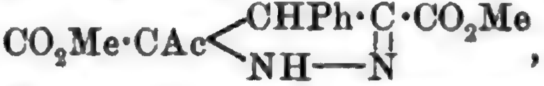
produced by adding bromine to a chloroform solution of selenoantipyrine, crystallises in lustrous, yellow needles and melts at 139°.

Selenoantipyrine dibromide, $C_{11}H_{12}N_2Br_2Se$, results from the action of hydrogen bromide on selenoantipyrine trioxide, and is also produced on evaporating the aqueous solution of the tetrabromide; it forms orange-red needles and melts at 236°; the *diiodide*, $C_{11}H_{12}N_2I_2Se$, separates from alcohol or chloroform in brown crystals and melts at 144°.

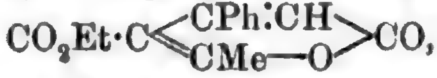
4-*Methylselenoantipyrine* (1-*phenyl*-2:3:4-*trimethyl*-2:5-*selenopyrazole*),  $\begin{array}{l}\text{CMe}{=}\text{NMe}\\ |\;\;\text{Se}<\\ \text{CMe}{=}\text{C—}\end{array}\!>\text{NPh}$, obtained from 5-chloro-1-phenyl-3:4-dimethylpyrazole methiodide by the action of potassium hydroselenide in alcoholic solution, crystallises in slender, yellow needles and melts at 172°; it forms a trioxide and a *dichloride*, $C_{12}H_{14}N_2Cl_2Se$ (m. p. 207—208°).

G. T. M.

Derivatives of 1:2-Pyrone or Coumalin from Pyrazolines.

By EDUARD BUCHNER and HEINRICH SCHRÖDER (*Ber.*, 1902, **35**, 782—790. Compare Abstr., 1895, i, 250).—*Methyl 5-acetyl-4-phenylpyrazoline-3:5-dicarboxylate*,  $CO_2Me\cdot CAc<\begin{array}{l}CHPh\cdot C\cdot CO_2Me\\ NH{-}{-}N\end{array}$, is prepared when mol. proportions of methyl benzylideneacetoacetate and methyl diazoacetate are heated together for 4 days at 45—60°, and forms crystals melting at 103°; the *phenylhydrazone*, $C_{21}H_{22}O_4N_4$, is a yellow, crystalline powder melting and decomposing at 155—157°. When the corresponding ethyl ester is treated with bromine in chloroform solution, ethyl 4-phenylpyrazole-3:5-dicarboxylate (m. p. 96°) is formed (this vol., i, 236).

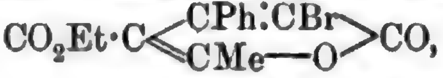
Ethyl 4-phenyl-6-methyl-1:2-pyrone-5-carboxylate,



$$CO_2Et\cdot C<\begin{array}{l}CPh{:}CH\\ CMe{-}O\end{array}>CO,$$

is obtained when ethyl 5-acetyl-4-phenylpyrazolinedicarboxylate is gradually heated from 160° to 230° in carbon dioxide, and the product fractionated under reduced pressure; it crystallises in colourless, lustrous needles melting at 104°. When boiled with aqueous sodium hydroxide, β-phenylglutaconic acid (m. p. 154°) is formed, together with acetic acid. *β-Phenylglutaconic anhydride* is obtained when β-phenylglutaconic acid is heated with acetyl chloride, and crystallises in lustrous leaflets decomposing at 197—199°.

Ethyl 3-bromo-4-phenyl-6-methyl-1:2-pyrone-5-carboxylate,



$$CO_2Et\cdot C<\begin{array}{l}CPh{:}CBr\\ CMe{-}O\end{array}>CO,$$

prepared by the action of bromine on ethyl phenylmethyl-1:2-pyronecarboxylate, crystallises in long, colourless needles melting at 72°. By the action of concentrated potassium hydroxide, it is converted into *3-phenyl-5-methylfurfuran-2:4-dicarboxylic acid*, $C_4OPhMe(CO_2H)_2$, which crystallises in colourless needles melting and decomposing at 224°. On boiling the brominated ester with 40 per cent. potassium hydroxide, *3-phenyl-5-methylfurfuran* is obtained, crystallising in colourless, hair-like needles melting at 80—81°.

Methyl 4-methyl-5-acetylpyrazoline-3:5-dicarboxylate was prepared from methyl ethylideneacetoacetate and methyl diazoacetate, and formed colourless crystals melting at 85°. When heated, it is converted into methyl 4:6-dimethyl-1:2-pyrone-5-carboxylate (m. p. 67°). By the action of bromine, the latter is brominated, yielding *methyl 3-bromo-4:6-dimethyl-1:2-pyrone-5-carboxylate*, which crystallises in long, colourless needles melting at 135°. K. J. P. O.

Action of Formaldehyde on *p*-Nitroaniline.

By JACOB MEYER and OTTO STILLICH (*Ber.*, 1902, **35**, 739—746. Compare Abstr., 1900, i, 222).—*5-Nitro-2-aminobenzyl-p-nitroaniline*,

$$NO_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot C_6H_3(NO_2)\cdot NH_2,$$

prepared by treating a solution of *p*-nitroaniline in concentrated acetic and sulphuric acids with 40 per cent. formaldehyde solution, crystallises from acetone or glacial acetic acid in oblique prisms melting at 227—228°. Its *monoacetyl* derivative, obtained by warming the base with acetic anhydride and sulphuric acid, crystallises in long, yellow needles and melts at 241—242°; it is accompanied by another substance melting at 280°, which, when heated with water, evolves acetic acid and yields the monoacetyl compound. *Diacetyl-5-nitro-2-aminobenzyl-*p*-nitroaniline*, produced by boiling the base with 4 parts of acetic anhydride, separates from alcohol in white, crystalline aggregates and melts at 210—211°.

*5-Nitro-2-methylaminobenzyl-*p*-nitroaniline*,

$$NO_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot C_6H_3(NO_2)\cdot NHMe,$$

a bye-product in the preceding formaldehyde condensation, crystallises from acetone or glacial acetic acid.

The two substituted benzyl-*p*-nitroanilines are hydrolysed by 40 per cent. sulphuric acid, yielding *p*-nitroaniline, but the methylated base is only partially decomposed.

*Diacetyl-5-nitro-2-methylaminobenzyl-*p*-nitroaniline*,

$$NO_2\cdot C_6H_4\cdot NAc\cdot CH_2\cdot C_6H_3(NO_2)\cdot NMeAc,$$

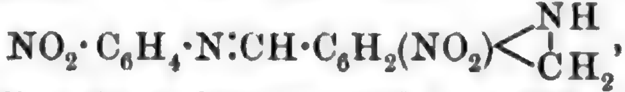
crystallises from ethyl acetate in prismatic needles and melts at 216—218°; this substance does not evolve hydrogen when treated with sodium in toluene, and hence it is concluded that the parent base has the constitution indicated.

*5-Nitro-3-hydroxymethyl-2-aminobenzylidene-*p*-nitroaniline*,

$$NO_2\cdot C_6H_4\cdot N{:}CH\cdot C_6H_2(NO_2)(CH_2\cdot OH)\cdot NH_2,$$

is also produced in the condensation between formaldehyde and *p*-nitroaniline in glacial acetic acid; it crystallises from alcohol in yellow, right-angled prisms and melts at 207—208°; the *monoacetyl* derivative, obtained by heating the base for 30 minutes with acetic anhydride, crystallises from alcohol in white needles and melts and decomposes at 223—225°. This benzylidene derivative is hydrolysed even by 8 per cent. sulphuric acid.

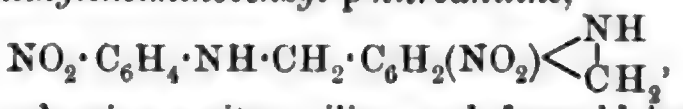
*5-Nitro-3 : 2-methyleneiminobenzylidene-*p*-nitroaniline*,



$$NO_2\cdot C_6H_4\cdot N{:}CH\cdot C_6H_2(NO_2){<}\begin{matrix}NH\\|\\CH_2\end{matrix},$$

produced by boiling the hydroxy-methyl base with glacial acetic acid, crystallises from acetone in heavy, golden-yellow plates and melts at 243—246°; it does not react with acetic anhydride even on prolonged heating.

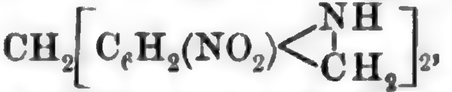
*5-Nitro-3 : 2-methyleneiminobenzyl-*p*-nitroaniline*,



$$NO_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot C_6H_2(NO_2){<}\begin{matrix}NH\\|\\CH_2\end{matrix},$$

produced by condensing *p*-nitroaniline and formaldehyde in glacial acetic acid containing half its weight of concentrated sulphuric acid, was, however, only obtained in one experiment; it separates in acicular aggregates and melts at 219—222°.

5 : 5′-Dinitro-3 : 2 : 3′ : 2′-dimethyleneiminodiphenylmethane,



$$CH_2\left[C_6H_2(NO_2){<}\begin{matrix}NH\\|\\CH_2\end{matrix}\right]_2,$$

prepared by heating *p*-nitroaniline and formaldehyde with concentrated hydrochloric acid and saturating the mixture with hydrogen chloride, crystallises from glacial acetic acid in needles and melts at 250—251°; its acetyl derivative is insoluble.

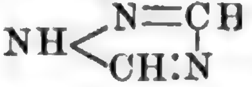
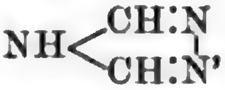
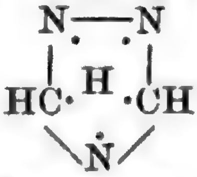
G. T. M.

Derivatives of Triazan. IV. By HUGO VOSWINCKEL (*Ber.*, 1902, **35**, 689).—The compounds, $C_8H_9ON_3$, $C_8H_{11}ON_3$, $C_{15}H_{14}O_2N_4$, $C_8H_8ON_3Cl$, and $C_8H_{10}ON_2Cl$, of Bamberger, Grob, and Free (this vol., i, 246, 247, 248) are identical with substances already described by the author (Abstr., 1899, i, 958; 1901, i, 53, 617), although formulated differently. T. M. L.

Voswinckel's Triazan Derivatives. By EUGEN BAMBERGER (*Ber.*, 1902, **35**, 756—759. See preceding abstract).—The author shows that the triazan derivatives described by Voswinckel (Abstr., 1899, i, 958) are identical with phenylazoacetaldoxime and its derivatives described by himself and Grob (this vol., i, 247). The author claims that his interpretation of the constitution of these compounds is correct.

R. H. P.

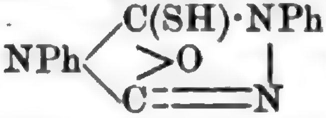
Triazan Derivatives. By HUGO VOSWINCKEL (*Ber.*, 1902, **35**, 1009—1012).—The author admits that the formulæ given by Bamberger (preceding abstract) for the substances originally prepared by himself are probably more correct than those first suggested (Abstr., 1899, i, 958). The ring formulæ for the reduction products are, however, still retained. J. J. S.

Formula of Triazole. I. and II. By GUIDO PELLIZZARI (*Atti R. Accad. Lincei*, 1901, [v], **10**, ii, 297—303; and 1902, [v], **11**, i, 20—23).—The four possible triazoles may be classified in two pairs, the two members of each pair corresponding with one and the same nucleus. In the present communication, the author deals with 1 : 2 : 4-triazole,  $NH<\genfrac{}{}{0pt}{}{N=CH}{CH:N}$, and 1 : 3 : 4-triazole,  $NH<\genfrac{}{}{0pt}{}{CH:N}{CH:N}$, which he considers to be identical compounds. The substance known as 1 : 2 : 4-triazole has been obtained by the following six methods, of which only the first two point to the 1 : 2 : 4-constitution, whilst the others are explained equally well by the 1 : 2 : 4- or the 1 : 3 : 4-formula. (1) Oxidation of 1-phenyl-1 : 2 : 4-triazole by means of acid potassium permanganate. (2) Heating of 1 : 2 : 4-triazolecarboxylic acid. (3) Reduction of urazole by means of phosphorus pentasulphide. (4) Action of formamide on formylhydrazide. (5) From thiosemicarbazide. (6) Action of nitrous acid on tetrazoline. The author finds that the product obtained by oxidising 1-phenyl-1 : 3 : 4-triazole with potassium permanganate in acid solution is identical with that obtained from 1-phenyl-1 : 2 : 4-triazole. The two triazoles, 1 : 2 : 4- and 1 : 3 : 4-, are hence represented by the formula , in which the positions of the double linkings will depend on where the iminic hydrogen is situated. T. H. P.

Constitution of Phenylurazole. By MAX BUSCH (*Ber.*, 1902, **35**, 971—972).—A claim for priority (compare Acree, this vol., i, 242).

R. H. P.

Molecular Transformation in the Urazole Series. By MAX BUSCH (*Ber.*, 1902, 35, 973—976).—When heated at 220—221°, the compound



$NPh\left<\begin{matrix}C(SH)\cdot NPh\\ >O \quad | \\ C=\!=\!=N\end{matrix}\right.$

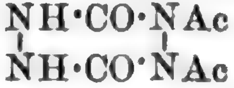
(Abstr., 1901, i, 235) is transformed into 1 : 4-diphenyl-5-thiourazole. Various analogous compounds, previously described (*loc. cit.*), undergo similar transformations.

R. H. P.

***p*-Diketohexahydrotetrazine and *p*-Diketothiohexahydrotetrazine. II.** By ATTILIO PURGOTTI and G. VIGANÒ (*Gazzetta*, 1901, 31, ii, 550—566. Compare Abstr., 1897, i, 640).—Attempts to prepare 1 : 2 : 4 : 5-tetrazine from *p*-urazine by reduction with phosphorus pentasulphide have as yet proved unsuccessful.

The action of hydrazodicarbonamide on phenylhydrazine yields phenylurazole in large quantity, and possibly also phenyl-*p*-urazine, but the latter could not be separated in a pure condition.

Diacetyl-p-*urazine*,



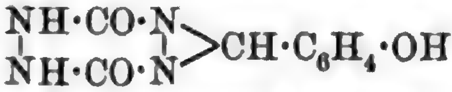
$\begin{matrix}NH\cdot CO\cdot NAc\\ | \qquad\quad | \\ NH\cdot CO\cdot NAc\end{matrix}$

, is obtained as a thick, yellow syrup, soluble in water but insoluble in alcohol or ether; on evaporating its solution, it yields the corresponding *monoacetyl* derivative, $C_4H_6O_3N_4$, separating in small, white scales which decompose without melting at 235°, and are soluble in water, alcohol, or ether.

With methyl iodide, *p*-urazine forms a dimethiodide, $C_2H_4O_2N_2,2MeI$, which separates from water in white plates dissolving slightly in alcohol or ether and decomposing at 200°.

p-Urazine (1 mol.) reacts with aldehydes (1 mol.), and with either 1 or 2 mols. of ketones.

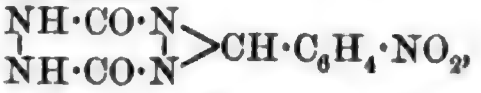
Salicylidene-p-*urazine*,



$\begin{matrix}NH\cdot CO\cdot N\\ | \qquad\quad | \\ NH\cdot CO\cdot N\end{matrix}>CH\cdot C_6H_4\cdot OH$

, is deposited from alcohol in white, shining leaflets which melt at 219° and dissolve slightly in ether, but are insoluble in water.

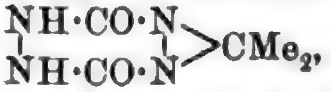
m-*Nitrobenzylidene*-p-*urazine*,



$\begin{matrix}NH\cdot CO\cdot N\\ | \qquad\quad | \\ NH\cdot CO\cdot N\end{matrix}>CH\cdot C_6H_4\cdot NO_2$

, forms minute crystals soluble in ether, but insoluble in water or alcohol.

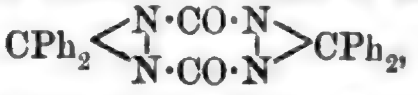
β-Propylidene-p-*urazine*,



$\begin{matrix}NH\cdot CO\cdot N\\ | \qquad\quad | \\ NH\cdot CO\cdot N\end{matrix}>CMe_2$

, separates in small, white scales, which melt at 203—204°, giving a yellow liquid, and are soluble in water or alcohol but almost insoluble in ether or acetic acid.

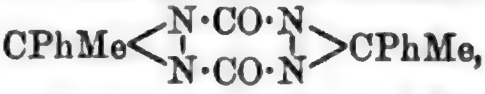
Dibenzophenone-p-*urazine*,



$CPh_2<\begin{matrix}N\cdot CO\cdot N\\ | \qquad | \\ N\cdot CO\cdot N\end{matrix}>CPh_2$

, crystallises from ether in pale yellow, monoclinic scales [$a : b : c = 4\cdot0054 : 1 : 2\cdot9889$; $\beta = 85°29\frac{1}{2}'$], which melt at 164° and are soluble in acetic acid.

Diacetophenone-p-*urazine*,



$CPhMe<\begin{matrix}N\cdot CO\cdot N\\ | \qquad | \\ N\cdot CO\cdot N\end{matrix}>CPhMe$

, separates from alcohol in yellow, monoclinic crystals [$a : b : c = 1\cdot3310 : 1 : 1\cdot1675$; $\beta = 76°17'$], which melt at 124° and are soluble in ether, acetone, chloroform, or acetic acid.

Dithio-p-*urazine hydrochloride*, $C_2H_4N_4S_2,HCl$, prepared by boiling dithiohydrazodicarbonamide with alcoholic hydrazine hydrate and precipitating the product with hydrochloric acid, crystallises from water in white, shining needles melting at 231—232°. *Dithio*-p-*urazine*,

$$CS<\begin{matrix}NH\cdot NH\\NH\cdot NH\end{matrix}>CS,$$

obtained from the hydrochloride by the action of barium hydroxide, separates in small, white crystals melting at 198—199°; it has a faint alkaline reaction, dissolves readily in water and to a slight extent in alcohol, and reacts with aldehydes. The *silver* salt, $C_2H_3N_4S_2Ag$, crystallises from water in white leaflets. *Benzylidenethio*-p-*urazine* separates from alcohol in yellow crystals which melt at 215° and decompose at 220°. *Salicylidenedithio*-p-*urazine* forms yellow crystals melting and decomposing at 226°. T. H. P.

α- and β-Naphthyldiguanide. By ALOIS SMOLKA and ED. HALLA (*Monatsh.*, 1901, **22**, 1146—1164. Compare Abstr., 1889, 951).—*α-Naphthyldiguanide*, formed from dicyanodiamide and α-naphthylamine hydrochloride, crystallises from dilute alcohol in nacreous leaflets which contain $\frac{1}{2}H_2O$ and melt at 158°. The following salts have been prepared: the *monohydrochloride*, $C_{12}H_{13}N_5,HCl$, which crystallises from dilute alcohol in white needles; the *dihydrochloride*, $C_{12}H_{13}N_5,2HCl$, formed by boiling the monohydrochloride with hydrochloric acid; the *mononitrate*, $C_{12}H_{13}N_5,HNO_3$, delicate needles from water; the *monosulphate*, $(C_{12}H_{13}N_5)_2,H_2SO_4,1\frac{1}{2}H_2O$, which loses its water at 120°; the *platinichloride*, $C_{12}H_{13}N_5,H_2PtCl_6$, precipitated by addition of hydrochloric acid and platinum chloride to the monohydrochloride. The copper compounds of α-naphthyldiguanide are rose-red, but in the anhydrous state violet. Being only slightly soluble in hot alcohol and less so in water, they do not crystallise easily. On prolonged boiling with water they become brown and are partially decomposed. Copper α-naphthyldiguanide, $(C_{12}H_{12}N_5)_2Cu,2H_2O$, is precipitated from a solution of the monohydrochloride and copper sulphate on addition of sodium hydroxide.

Copper-α-naphthyldiguanide hydrochloride,

$$(C_{12}H_{12}N_5)_2Cu,2HCl,2\tfrac{1}{2}H_2O,$$

is formed by addition of an alcoholic solution of the diguanide to an aqueous solution of cupric chloride. The salt separates in crusts on spontaneous evaporation of the solution. Copper-α-naphthyldiguanide nitrate, $(C_{12}H_{12}N_5)_2Cu,2HNO_3$, is precipitated by addition of cupric nitrate solution to an alcoholic solution of the diguanide. Copper-α-naphthyldiguanide sulphate $(C_{12}H_{12}N_5)_2Cu,H_2SO_4,2H_2O$, is precipitated by addition of sodium sulphate to a dilute alcoholic solution of the diguanide copper hydrochloride.

β-Naphthyldiguanide and its derivatives are prepared by the same methods; they are more stable and crystallise more easily than the corresponding α-compounds. β-Naphthyldiguanide crystallises from boiling water in thin, glistening leaflets which melt at 180° with evolution of gas. The following salts have been prepared: the *monohydrochloride*; the *mononitrate*; the *mono-* and *di-sulphates*, $(C_{12}H_{13}N_5)_2H_2SO_4,\frac{1}{2}H_2O$ and $C_{12}H_{13}N_5,H_2SO_4$; the *platinichloride*.

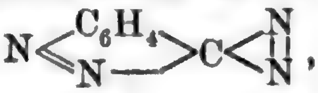
Copper-β-naphthyldiguanide is precipitated from the solution of its hydrochloride by addition of sodium hydroxide. The hydrochloride, $(C_{12}H_{12}N_5)_2Cu,2HCl,2H_2O$; the nitrate, $(C_{12}H_{12}N_5)_2Cu,2HNO_3$; and the sulphate, $(C_{12}H_{12}N_5)_2Cu,H_2SO_4,1\frac{1}{2}H_2O$, have been prepared.

With nickel salts, β-naphthyldiguanide forms slightly soluble, yellow compounds. G. Y.

Alkylation of Phenylazoacetaldoxime. By EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1902, **35**, 746—756. See this vol., i, 247).—When treated with methyl iodide and sodium methoxide, phenylazoacetaldoxime yields 1-phenyl-3-methyltriazole. The N-*methyl ether* of the oxime, $\mathrm{NPh{:}N{\cdot}CMe}<\begin{matrix}\mathrm{O}\\ |\\ \mathrm{NMe}\end{matrix}$, obtained by the action of diazomethane on the oxime, or of methyl iodide on its sodium derivative, crystallises in long, silky, orange needles from water, melts at 96—96·5°, and has no odour; when heated with sodium methoxide, it yields 1-phenyl-3-methyltriazole, and, when reduced, a mixture of aniline and phenylhydrazine. The O-*methyl ether*, $\mathrm{NPh{:}N{\cdot}CMe{:}N{\cdot}OMe}$, obtained by the action of methyl iodide on the silver salt, is an orange-coloured oil, which solidifies at the temperature of a mixture of ice and salt, boils at 133—134° under 12 mm. pressure, is insoluble in water, and has a very characteristic sweet odour.

When the O-methyl ether is treated with concentrated hydrochloric acid, it yields the *hydrochloride* of *p*-chlorophenylhydrazoacetaldoxime methyl ether, which crystallises in glistening, yellowish-white leaflets; this, when treated with potassium acetate, forms p-*chlorophenylazoacetaldoxime methyl ether*, which crystallises in slender, golden, silky needles melting at 75·5—76°.

The O-*ethyl ether* of the oxime crystallises in orange-yellow, lustrous leaflets, melts at 39—39·5°, and has a characteristic odour; the iso*propyl ether* is a bright red oil; both these ethers react with hydrochloric acid in a manner similar to the methyl ether. R. H. P.

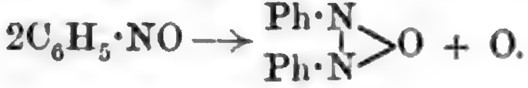
Quinonoid Diazo-compounds and the so-called Triazolens. By ARTHUR HANTZSCH (*Ber.*, 1902, **35**, 888—896).—The diazo-compound from *p*-aminodiphenylamine (Ikuta, Abstr., 1888, 467; Jacobson, Abstr., 1896, i, 23) resembles the aniline derivatives in that it forms a neutral diazonium chloride. It gives a yellow *potassium anilinobenzeneazosulphonate*, $NHPh{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_3K$, with potassium hydrogen sulphite in the normal way; the *silver* salt is a dark red precipitate; the *acid* crystallises in glistening red prisms and forms a *hydrochloride*, $C_{12}H_{11}N_3SO_3,HCl$; the *phenylsulphone*, $NHPh{\cdot}C_6H_4{\cdot}N_2{\cdot}SO_2Ph$, from the diazonium sulphate and sodium benzenesulphinate forms red crystals, melts at 82°, and does not dissolve in water, but is soluble in organic solvents. The action of potassium cyanide also proceeds normally, giving an *anilinobenzeneazocyanide*, $NHPh{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CN$, which forms a carmine-red powder, melts at 129°, and does not dissolve in water but dissolves in organic solvents. The action of potassium hydroxide gives rise to a compound which is regarded as *phenyliminoquinone diazide*, $\mathrm{NPh{:}C_6H_4}<\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}$; it forms a grey-brown powder and very readily decomposes. This type of diazo-compound has only been known hitherto in the so-called diazophenols, $O\colon C_6H_4\colon N_2$ (Wolff, *Annalen*, 1900, **312**, 126), of which the above compound would be the phenylimino-derivative, but a similar constitution,  $N\begin{matrix}\diagup C_6H_4\diagdown\\ \diagdown N\text{——}\diagup\end{matrix}C<\begin{matrix}N\\ \|\\ N\end{matrix}$, is now suggested for the triazolens.

The *diazochloride* of dimethyl-*p*-phenylenediamine was also prepared, but could not be converted into a compound of the above type; monomethyl-*p*-phenylenediamine could not be converted into a diazo-compound, as nitrogen was vigorously given off even below 0°.

T. M. L.

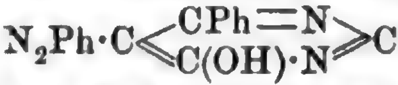
Azotates of the Fatty Series. By Arthur Hantzsch and Martin Lehmann (*Ber.*, 1902, **35**, 897—905).—*Potassium methylazotate*, $CH_3\cdot N\colon N\cdot OK,H_2O$, the first metallic diazotate which has been isolated in the fatty series, separates in white scales on shaking nitrosomethylurethane with concentrated aqueous potassium hydroxide; it is very unstable in presence of moisture, and on heating decomposes partially into diazomethane and potassium hydroxide; a similar decomposition occurs with explosive violence on adding a drop of water to a mass of the salt. The *rubidium* and *sodium* salts are similarly constituted, but are less readily purified. The *alcoholate*, $CH_3\cdot N\colon N\cdot OK,EtOH$, is formed as a white precipitate by the action of potassium ethoxide on ethereal nitrosomethylurethane.

Potassium benzylazotate, $CH_2PH\cdot N\colon N\cdot OK,H_2O$, is a white salt, but rapidly turns reddish owing to partial decomposition. The *alcoholate*, $CH_2Ph\cdot N\colon N\cdot OK,EtOH$, forms a white, crystalline powder, and when moistened with water decomposes into benzyl ethyl ether and stilbene. *Phenyldiazomethane*, $CHPh<\begin{matrix}N\\ \|\\ N\end{matrix}$, which Pechmann was not able to isolate, was obtained as a reddish-brown oil by cautiously warming nitrosobenzylmethane with concentrated potassium hydroxide. When distilled, it loses nitrogen and is converted into stilbene; with water, it gives benzyl alcohol, and with alcohol benzyl ethyl ether.

When treated in a similar manner, nitrosobenzene and nitrosodimethylaniline are converted into the azoxy-compounds,  $2C_6H_5\cdot NO\longrightarrow\begin{matrix}Ph\cdot N\\ \|\\ Ph\cdot N\end{matrix}>O+O$.

T. M. L.

Action of Diazo-compounds on the Esters of 2-Acyl-1 : 3-ketonic Acids. By Carl Bülow and Ekkehard Hailer (*Ber.*, 1902, **35**, 915—938).—By the action of diazobenzene chloride on ethyl diacetylacetate or acetylpropionylacetate, an acetyl or propionyl group is eliminated, and an ethyl phenylazoacetoacetate is produced identical with that prepared from diazobenzene chloride and ethyl acetoacetate. The *acetyl* derivative, $NPhAc\cdot N\colon CAc\cdot CO_2Et$, prepared by warming the azo-compound with zinc chloride and acetic anhydride, crystallises from alcohol in colourless prisms, melts at 119—120°, and gives acetanilide when reduced with zinc dust and dilute sulphuric acid.

Ethyl phenyleneazobenzoylacetate is formed by loss of an acetyl group when ethyl acetylbenzoylacetate is treated with diazobenzene chloride. The *amide*, $NHPh\cdot N\colon CBz\cdot CO\cdot NH_2$, crystallises from alcohol in yellow flakes or needles and melts at 163—165°. 4-*Hydroxy-5-benzeneazo*-2 : 6-*diphenyl*-1 : 3-*diazine*,  $N_2Ph\cdot C\left\langle\begin{matrix}CPh=N\\ C(OH)\cdot N\end{matrix}\right\rangle CPh$, prepared from the azo-ester and benzamidine hydrochloride, crystallises from alcohol in long, golden-yellow, glistening needles and melts at 138—139°. The *acetyl* derivative of the azo-ester, $NAcPh\cdot N\colon CBz\cdot CO_2Et$, crystallises from alcohol in rosettes of minute, white, silky needles, melts at 151°, and yields acetanilide when reduced.

Ethyl o-*tolylazobenzoylacetate*, $C_7H_7\cdot N_2\cdot CHBz\cdot CO_2Et$, prepared by the action of *o*-diazotoluene chloride on ethyl benzoylacetate or ethyl acetylbenzoylacetate, crystallises from alcohol in yellowish-red prisms and melts at 86°. A similar displacement of the acetyl group occurs in the interaction of *p*-nitrodiazobenzene chloride with ethyl acetylbenzoylacetate (compare Stierlin, Abstr., 1888, 1088 and 1298).

Ethyl diphenylbisazobenzoylacetate, $C_{12}H_8(N_2\cdot CHBz\cdot CO_2Et)_2$, from diazotised benzidine and ethyl acetylbenzoylacetate, separates as a yellow powder, but crystallises from acetic acid in stout, red prisms; the yellow modification becomes red at 180°, and both forms melt at 187°. It condenses with phenylhydrazine to a *compound*, $C_{38}H_{30}O_4N_6$, in which one of the acetoacetate groups is converted in the normal way into a pyrazolone; this separates in small, red crystals from the acetic acid solution and melts at 215°.

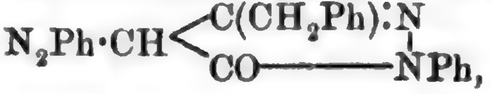
Ethyl carboxyphenylazobenzoylacetate,

$$CO_2H\cdot C_6H_4\cdot N_2\cdot CHBz\cdot CO_2Et,H_2O,$$

from *o*-diazobenzoic acid and ethyl acetylbenzoylacetate, crystallises from alcohol in yellow needles and melts at 145—147°; the *ammonium* salt forms yellow flakes; the *sodium* and *silver* salts form hair-like, yellow needles. The *acid*, $C_{16}H_{12}O_5N_2$, obtained on hydrolysing the ester, is a yellow substance and melts at 220°. 4-*Carboxybenzeneazo*-1 : 3-*diphenylpyrazolone*, $C_{22}H_{16}O_3N$, prepared by the action of phenylhydrazine on the ester, crystallises from acetic acid in hair-like, felted needles and melts at 276°. 4-*Carboxybenzeneazo*-3-*phenyl*-5-isoo*xazolone*, prepared by the action of hydroxylamine hydrochloride on the ester, separates from acetic acid in yellow needles and melts at 245—250°.

4-*Sulphobenzeneazo*-1 : 3-*diphenylpyrazolone*, $C_{21}H_{16}O_4N_4S$, prepared by the action of phenylhydrazine on the product from diazotised sulphanilic acid and ethylacetylbenzoylacetate, forms dark red prisms or needles and melts and decomposes at 275°.

Ethyl acetylphenylacetylacetate, $CH_2Ph\cdot CO\cdot CHAc\cdot CO_2Et$, prepared in an impure state by Fischer and Bülow (Abstr., 1885, 1237), is a yellowish liquid and boils with partial decomposition at 190° under 15 mm. pressure; the *copper* salt, $(C_{14}H_{15}O_4)_2Cu$, forms slender, blue, silky needles and melts at 182—183° to a brown liquid, dissolves readily in chloroform or in hot benzene, and crystallises from alcohol. When condensed with diazobenzene chloride and then with phenylhydrazine, it gives a 4-*benzeneazo*-1-*phenyl*-3-*benzylpyrazolone*,



$$N_2Ph\cdot CH\left\langle\begin{matrix}C(CH_2Ph)\colon N\\ CO\text{———}NPh,\end{matrix}\right.$$

which crystallises from acetic acid in yellowish-red needles and melts at 147°.

*Ethyl phenylazoacetyl-*p*-nitrobenzoylacetate,*

$$NO_2\cdot C_6H_4\cdot CO\cdot CH(N_2Ph)\cdot CO_2Et,$$

from diazobenzene chloride and ethyl acetyl-*p*-nitrobenzoylacetate, crystallises from alcohol in yellow flakes and melts and decomposes at 126—127°.

*Ethyl acetyl-*m*-nitrobenzoylacetate,* $NO_2\cdot C_6H_4\cdot CO\cdot CHAc\cdot CO_2Et$, crystallises from alcohol in stout, yellowish prisms and melts at 74—75°. *Ethyl* m*-nitrobenzoylacetate,* $NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2Et$, crystallises from alcohol in reddish-white prisms and melts at 78—79°. *Ethyl phenylazo-*m*-nitrobenzoylacetate,* $NO_2\cdot C_6H_4\cdot CO\cdot CH(N_2Ph)\cdot CO_2Et$, crystallises from alcohol in stout, yellowish-brown spangles and melts at 134—135°.

Ethyl acetylcinnamoylacetate (Fischer and Kuzel, Abstr., 1883, 587) and ethyl benzoylmalonate do not condense with diazobenzene chloride.

Ethyl phenylazodibenzoylacetate, $NPh_2\cdot CBz_2\cdot CO_2Et$, from ethyl dibenzoylacetate and diazobenzene chloride, crystallises from alcohol in slender, yellow prisms and melts at 116°.

Ethyl phenylacetylbenzoylacetate, $CH_2Ph\cdot CO\cdot CHBz\cdot CO_2Et$, decomposes when distilled in a vacuum; the *copper* salt crystallises from chloroform or alcohol in bluish needles and melts and decomposes at 194—195°; it condenses with *o*-diazobenzoic acid with elimination of the phenylacetyl group.

*Ethyl benzoyl-*p*-nitrobenzoylacetate,* $NO_2\cdot C_6H_4\cdot CO\cdot CHBz\cdot CO_2Et$, crystallises from alcohol in clusters of slender, white needles and melts at 86—87°. *Ethyl phenylazobenzoyl-*p*-nitrobenzoylacetate,*

$$NO_2\cdot C_6H_4\cdot CO\cdot CBz(N_2Ph)\cdot CO_2Et,$$

crystallises from alcohol in yellow needles and melts at 105°.

It is pointed out that where two aromatic acyl groups are attached to ethyl acetate, neither is displaced by the action of diazobenzene chloride; where one fatty and one aromatic group are present, the fatty group is displaced, and where two fatty groups are present, the higher member is displaced; this is probably connected with the strength of the acids, as the displaced groups are all derived from weaker acids than those which remain. Carbethoxy-groups are not displaced.

T. M. L.

Action of Sulphur Dioxide on *p*-Nitrodiazobenzene Hydroxide. By ALFRED EKBOM (*Ber.*, 1902, 35, 656—662).—p-*Nitrobenzenediazo-*p*-nitrobenzenesulphone,* $NO_2\cdot C_6H_4\cdot N_2\cdot SO_2\cdot C_6H_4\cdot NO_2$, is formed as a reddish-yellow precipitate on passing sulphur dioxide into an absolute alcoholic solution of *p*-nitrodiazobenzene hydroxide at −5° to 0°; it crystallises from warm ethyl acetate in microscopic needles, decomposes at 135°, is not acted on by light, and is also obtained by the interaction of *p*-nitrodiazobenzenesulphochloride with sodium *p*-nitrobenzenesulphinate. When heated with concentrated hydrochloric acid for 1—2 hours at 100°, it yields a mixture of *p*-chloronitrobenzene, *p*-dinitrodiphenylsulphoxide (m. p. 179—180°), and *p*-nitrobenzenesulphonic acid.

W. A. D.

Aromatic Diazonium Salts and Ammoniacal Cuprous Oxide Solution. By DANIEL VORLÄNDER and FELIX MEYER (*Annalen*, 1902, **320**, 122—144).—The action of cuprous oxide, dissolved in solutions of ammonia or hydroxylamine, on diazonium salts leads to the formation of azo- and diphenyl derivatives with the elimination of nitrogen. The course of the reaction occurring in the case of substituted aromatic amines depends on the saturated or unsaturated character of their substituents, and not on their negative or positive nature; the presence of unsaturated radicles favours the formation of diphenyl derivatives. The cuprous oxide solution employed is prepared either by dissolving cupric sulphate in excess of hydroxylamine or by treating an ammoniacal solution of this salt with a reducing agent such as hydroxylamine, sulphurous acid, or ferrous sulphate. The diazonium salts from aniline, *o*-, *m*-, and *p*-toluidine, 4-amino-*m*-xylene, *ψ*-cumidine, and mesidine, when treated with this reagent, give rise to the corresponding azo-compounds, the yields of 4-azo-*m*-xylene and azo-*ψ*-cumene being about 90 per cent. of the theoretical. The three chloroanilines and *p*-bromoaniline, when treated in a similar manner, furnish small quantities of their respective azo-derivatives.

Azo-compounds are also the chief products of reaction in the case of *o*-anisidine, *p*-aminophenol, and *p*-phenetidine, an almost quantitative yield being obtained from the first of these bases.

o-Nitroaniline, when diazotised and treated with the cuprous oxide solution, yields a small quantity of 2 : 2′-dinitrodiphenyl, together with a trace of *o*-nitrophenol; *p*-nitroaniline, on the other hand, gives an almost theoretical yield of 4 : 4′-dinitrodiphenyl accompanied by a slight amount of nitrobenzene. *p*-Aminobenzoic acid and its ethyl ester furnish their corresponding azo-compounds; ethyl *p*-azobenzoate crystallises in orange-coloured, rectangular plates melting at 144°; Fittica, who formerly obtained an azo-ester from ethyl *p*-nitrobenzoate, described it as crystallising in yellow, prismatic crystals melting at 88°. *m*-Aminobenzoic acid and its ester give rise to azo-compounds; it was not, however, found possible to convert the azo-acid produced into diaminodiphenic acid, and the azo-ester, which distils at 240° under 15 mm. pressure and crystallises in golden-yellow prisms melting at 108—109°, differs from the product described by Golubeff and by Fittica as melting either at 90—92° or at 97°.

When anthranilic acid is diazotised and treated with the cuprous oxide solution, it loses almost all its nitrogen, the principal product of reaction being diphenic acid; its methyl ester, under these conditions, yields methyl diphenate, whilst the ethyl salt gives rise to ethyl benzoate.

The action of ammoniacal cuprous oxide solution on *o*-diazobenzoic acid also leads to the formation of the following bye-products: phenol, salicylic acid, benzoic acid, and probably *o*-chlorobenzoic acid; *o*-azobenzoic acid, however, could not be distinguished. *o*-Diazobenzoic acid, when reduced with a suspension of copper powder in ammonia solution, furnishes a small quantity of diphenic acid; negative results are obtained when the copper or cuprous oxide is suspended in sodium hydroxide solution or when other reducing agents such as ferrous hydroxide are employed. Cuprous hydride, suspended either in ammoniacal or dilute sulphuric acid solution, reduces *o*-diazobenzoic acid to benzoic acid. G. T. M.

Decomposition of Diazonium Salts by the Aid of Alcohol.

By ARTHUR HANTZSCH (*Ber.*, 1902, **35**, 998—1001).—The *rationale* of the decomposition of diazonium salts has been previously discussed by the author (Abstr., 1900, i, 703), and fresh data and arguments are now adduced in favour of his original explanation and in opposition to Bamberger's more recent conception (this vol., i, 246). If Bamberger's view is accepted and the decomposition is preceded by the formation of a diazonium alkyloxide, $ArN_2 \cdot OEt$, then in the similar decomposition of diazonium salts by the aid of water it must be assumed that the decomposition is preceded by the formation of a diazonium hydroxide and free mineral acid; in other words, the salt is hydrolysed by the water. But it can be directly proved that the decomposition is not retarded by introducing acid at the beginning of the reaction and does not diminish in velocity as the amount of free acid formed increases, and thus the reaction is in no sense comparable with ordinary cases of hydrolysis.

Similarly, the decomposition of diazonium salts, for example, tribromodiazonium sulphate, under the influence of alcohol is not retarded by the presence of an excess of free acid, and cannot therefore be preceded by a decomposition effected by the alcohol. J. J. S.

Action of Cyanoacetic Esters and of their Substitution Derivatives on Diazonium and Tetra-azonium Chlorides.

By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], **27**, 104—124. Compare Abstr., 1899, i, 58).—The present paper contains a fuller account of the author's work in connection with this subject, some results of which have been already published. The substances obtained by the action of ethyl cyanoacetate on the tetra-azonium chlorides yield the stable *β*-modification when precipitated from alkaline solution by carbon dioxide, and it is also obtained by dissolving the *a*-ester in liquids of high boiling point (aniline, nitrobenzene, &c.). The unstable *a*-esters are obtained by precipitating the alkaline solutions of the *a*- or *β*-modification by hydrochloric acid, benzoyl chloride, or acetic anhydride (compare Krückeberg, Abstr., 1894, i, 369).

Ethyl diphenyldihydrazonecyanoacetate: the stable *β*-ester melts at 204—206°, the unstable *a*-ester at 234°. *Ethyl diphenyldimethylhydrazonecyanoacetate* is obtained by the action of methyl chloride on the sodium or silver derivative of the preceding compound, and forms yellow lamellæ which melt at 210—212°. *Ethyl diphenyldiethylhydrazonecyanoacetate* forms small, yellow crystals melting at 144—145°. *Ethyl diphenyldihydrazonemonobenzoylcyanoacetate* is obtained by boiling a mixture of xylene and benzoyl chloride in which is suspended the silver derivative of ethyl diphenyldihydrazonecyanoacetate; it melts at 198—200°.

Methyl diphenyldihydrazonecyanoacetate.—The *a*-ester, obtained in a manner similar to the corresponding ethyl ester, forms a yellow, crystalline powder which melts at 270°. The *β*-ester melts at 228—230°. When dissolved in boiling nitrobenzene, the *β*-ester is converted into the α-ester, which is, in this case, the stable form. *Methyl sodiodiphenyldihydrazonecyanoacetate* forms yellowish, crystalline needles, soluble in methyl alcohol, water, acetone, or pyridine. *Methyl diphenyldimethylhydrazonecyanoacetate* separates from its solution in nitrobenzene or aniline in microscopic needles melting at 276—277°. *Ethyl di-o-tolyldihydrazonecyanoacetate*: The β-ester, obtained by the action of ethyl cyanoacetate on tetrazoditolyl, melts at 224—226°; the α-ester is obtained by precipitation of the alkaline solutions of the ester with hydrochloric acid. *Ethyl sodiodi-o-tolyldihydrazonecyanoacetate* forms reddish, crystalline needles soluble in acetone or aqueous alcohol. *Ethyl di-o-tolyldimethylhydrazonecyanoacetate* crystallises in faintly yellow plates melting at 220—222°. *Ethyl di-o-tolylhydrazonemonobenzoylcyanoacetate*, obtained similarly to the diphenyl compound, forms orange crystals melting at 229—230°. *Methyl di-o-tolyldihydrazonecyanoacetate*: the α-modification, which is the stable one, separates from its solution in nitrobenzene in small, reddish crystals melting at 270—272°. The β-ester melts at 225—227°. *Methyl sodiodi-o-tolyldihydrazonecyanoacetate* forms reddish needles soluble in water, alcohol, acetone, or pyridine. *Methyl di-o-tolyldimethylhydrazonecyanoacetate* crystallises from its solution in nitrobenzene and melts at 266—267°. *Di-o-tolyldihydrazonecyanoacetic acid*, obtained by the hydrolysis of the α- or β-ester, forms golden-yellow plates which melt at 243—244°. *Methyl di-o-anisyldihydrazonecyanoacetate*: The α-ester melts at 266—268°; the β-ester melts at 254—255°. *Methyl sodiodi-o-anisyldihydrazonecyanoacetate* forms small, yellow plates, insoluble in water and very slightly soluble in acetone or pyridine; it reacts neither with the alkyl iodides nor with the acyl chlorides. A. F.

Action of 2:6-Diamidomethylazobenzene on Benzaldehyde.

By Ferdinando Perucchetti (*Chem. Zeit.*, 1902, **26**, 28).—Methyldiamino-2:6-azobenzene condenses with the molecular proportion of benzaldehyde to form a triazine which may be regarded as the condensation product of the hypothetical hydrazone,

$$C_6H_5\cdot NH\cdot N\!:\!C_6H_2Me(NH)\cdot NH_2$$

[NH : Me : NH_2 = 2 : 3 : 4], with benzaldehyde. It is a white, difficultly crystallisable substance, which melts with decomposition at 200°. It is insoluble in water, alcohol, ether, or benzene, but is slightly soluble in toluene. It can be diazotised, and yields azo-dyes with resorcinol, β-naphthol, &c. The monoacetyl derivative is yellowish. No substances of a sweet taste are yielded on sulphonation (compare Noelting, Abstr., 1898, i, 155). A. F.

Action of Hydrogen Chloride on Diphenyl-*p*-azophenylene.

By Ernst Bandrowski and A. Prokopeczko (*Bull. Acad. Sci. Cracow*, 1901, 441—443).—By the action of dry hydrogen chloride on diphenyl-*p*-azophenylene in benzene solution in the cold, the authors obtained diphenyl-*p*-phenylenediamine hydrochloride and two isomeric *diphenylchlorophenylene-*p*-diamines* melting at 157° and 106° respectively. They yield two isomeric *diphenyldichloroazophenylenes*, which are crystalline substances of a fine red colour and melt at about 220°. The *azophenylene*, obtained from the diphenyldichlorophenylenediamine melting at 157°, yields with aniline the corresponding *azophenine*, $C_6Cl_2(NHPh)_2(NPh)_2$ [=1:4:2:5:3:6]. The diamine, therefore, contains two free para-positions, whereas the diamine of melting point 106° does not.

By the action of hydrogen chloride on the two dichloroazophenylenes, there is obtained, besides the chlorides of the corresponding dichlorodiamines, *diphenyltetrachlorophenylene*-p-*diamine*, $C_6Cl_4(NHPh)_2$, a white crystalline substance which is only slightly soluble in the ordinary organic solvents and has a very weak basic character. A. F.

Sulphur in Proteids. By KARL A. H. MÖRNER (*Zeit. physiol. Chem.*, 1902, **34**, 207—338).—In continuation of a research in which it was shown that horny substance when treated with hydrochloric acid gives a good yield of cystin (Abstr., 1900, i, 128), it is now shown that the same is true for a large number of other proteid substances. The yield naturally is not so large, as the total amount of sulphur is smaller than in horn, but the fraction of sulphur contained in the cystin-yielding portion of the molecule, although variable, is usually large. Other parts of the paper are concerned with the other sulphur combinations in the proteid molecule, and with a discussion of the results in reference to the molecular size of proteids. W. D. H.

Are Proteids, prepared in the usual way, combined with Fat or Fatty Acid. By E. R. POSNER and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, *Amer. J. Physiol.*, **6**, xxix).—Using Dormeyer's method on quantities of proteid and mucoid from 2 to 13 grams in weight, and following Nerking's procedure, the results were negative. W. D. H.

Preparation of Carbamide by the Oxidation of Albumin. By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1901, **34**, 28—31. Compare Abstr., 1901, i, 490).—In reply to Schulz (*ibid.*, i, 780), it is pointed out (1) that the oxidation must take place very slowly in order that trustworthy results may be obtained, (2) that water must be added during the boiling and that the volume of the liquid should never fall below two-thirds of the original, (3) that the precipitation with alcohol must be repeated until the carbamide is obtained free from salts. J. J. S.

Phosphoric Acid Esters from Egg-albumin. By HEINRICH BECHHOLD (*Zeit. physiol. Chem.*, 1901, **34**, 122—127).—When a solution of crystallised egg-albumin is shaken with phosphoryl chloride and sodium hydroxide or normal sodium phosphate, products are obtained which the author regards as true esters of phosphoric acid. A part of these are precipitated on the addition of acetic acid, the remainder on warming. The percentage of phosphorus varies somewhat. J. J. S.

Detection of Glucosamine and an Acid derived from an Aminohexose among the Hydrolytic Products of Serum-albumin. By LEO LANGSTEIN (*Ber.*, 1902, **35**, 176—178).—The precipitate obtained by alcohol from a solution of serum-albumin in alkali was treated with 5 per cent. sulphuric acid, and from the resulting solution glucosamine was separated in the form of its pentabenzoyl derivative. The syrup left after precipitation with alcohol, when treated with hydrochloric acid, yielded an *acid* which gave the Molisch reaction, and formed insoluble *barium*, *calcium*, and *lead* salts, and a *benzoyl* derivative, which yielded a *potassium* salt crystallising in yellow nodules. R. H. P.

Action of Sodium Ethoxide on Chlorinated Casein. By THEODOR PANZER (*Zeit. physiol. Chem.*, 1901, **34**, 66—82).—When chlorocasein (Abstr., 1901, i, 780) is treated with an alcoholic solution of sodium ethoxide, part of the chlorine is removed in the form of sodium chloride and a number of simpler products are formed. Among the substances soluble in alcohol is *chlorocaseonic acid*, containing C = 50·81, H = 5·74, N = 11·43, Cl = 9·02, and O = 23·00 per cent. It dissolves in alcohol, but is precipitated by water, and is also insoluble in ether, benzene, or chloroform. It has not been obtained in a crystalline state and its solutions in alkalis do not coagulate when warmed. It dissolves in cold sodium chloride solutions, but is reprecipitated on warming and again dissolves as the liquid cools. It does not give the more common reactions for proteids, and when hydrolysed with hydrochloric acid yields neither tyrosine nor glutamic acid. J. J. S.

Electrolysis of Nucleohiston and Histon Salts. By W. HUISKAMP (*Zeit. physiol. Chem.*, 1901, **34**, 32—54).—When an aqueous solution of sodium nucleohiston (Abstr., 1901, ii, 461) is subjected to electrolysis, using platinum electrodes, free nucleohiston is almost quantitatively deposited on the anode and practically no secondary reactions occur. The results agree with the view that sodium nucleohiston is ionised in aqueous solutions, but are also, to a certain extent, compatible with the view that the electrolysis is really due to small amounts of mineral salts present as impurities.

Aqueous solutions of histon sulphate prepared by dialysis give the usual sulphion reactions, indicating that the salt is ionised in its aqueous solution. When solutions of histon salts are dialysed for some time, they become faintly alkaline to litmus but not to phenolphthalein, indicating that a certain amount of hydrolysis has taken place. When subjected to electrolysis, histon salts deposit histon on the cathode. Experiments made with casein, globin, and other proteids gave similar results.

When a solution of sodium nucleohiston is added to histon hydrochloride, a precipitate is obtained which probably consists of a compound of nucleohiston and histon; the percentage of ash in the precipitate is only 1·75—1·85.

The fact that sodium nucleohiston is less soluble in solutions containing free sodium ions is in agreement with the ionisation of the salt. J. J. S.

Organic Chemistry.

New Synthesis of Methane. By Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1902, **134**, 514—516. Compare Abstr., 1901, i, 195).—When a mixture of carbon monoxide (1 vol.) and hydrogen (3 vols.) is passed over reduced nickel at 250°, the two gases are completely converted into methane and water. Carbon dioxide and hydrogen similarly react in the presence of reduced nickel at a somewhat higher temperature, yielding only methane and water.

K. J. P. O.

Commercial "Benzine." By A. M. Rabinovitsch (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 200—201).—The author has submitted to distillation four samples of Russian "benzine" obtained from different sources and having sp. gr. (at 15°/15°) lying between 0·7084 and 0·72095. Of the four fractions distilling: (1) up to 70°, (2) from 70—90°, (3) from 90—100°, and (4) above 100°, the second is in all cases the largest, but the different samples vary considerably in the proportions existing between the fractions. The flash points all lie within the limits − 10° and − 12°.

T. H. P.

Commercial Kerosenes from Kieff. By D. Kudisch (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 201—202).—The author has examined six samples of commercial kerosene having sp. gr. varying from 0·82300 to 0·82368. The percentages by volume distilling over at different temperatures are: from 137—150°, 5·0 to 6·0; 150—200°, 31·0 to 36·0; 200—270°, 45·5—47·5; above 270°, 13·0 to 15·5. The viscosity at 20° varies from 1·0636 to 1·0727 and at 1° from 1·1909 to 1·205. The flash point limits are 32·5° and 36·0°. All the samples are readily and completely soluble in absolute alcohol and give no solid products when cooled to − 20°. The percentages of sulphur in the oils lie between 0·0045 and 0·005°. These data are all in accord with those yielded by good kerosenes.

T. H. P.

The Wax of Algæ and its relation to Petroleum. By Gustav Kraemer and Adolf Spilker (*Ber.*, 1902, **35**, 1212—1223. Compare Abstr., 1900, i, 73).—Wax is present in all specimens of peat, brown coal, &c., in varying quantities and contains very various amounts of sulphur which owes its origin to the oxidising action of sulphur bacteria. In some cases, the wax is derived from green algæ, and is not then accompanied by siliceous skeletons. When the wax is distilled, it first froths up and evolves carbon dioxide, carbon monoxide, hydrogen sulphide and water containing small amounts of fatty acids in solution. If the distillation be carried out under the ordinary pressure, this stage is followed by the evolution of methane, olefines, and carbon dioxide, whilst a semi-liquid mass of paraffins distils over.

Under diminished pressure, on the other hand, no methane is evolved and a waxy mass, melting at 74—78°, distils over.

By extraction of the wax with alcohol, a fraction soluble in hot alcohol can be obtained which consists of free acid mixed with an ester. The hydrolysis of the wax yields an acid or mixture of acids melting at between 70° and 80° (the melting point varying according to the source of the wax), and corresponding in composition with a fatty acid containing about 22 carbon atoms. The alcoholic component of the ester is a white mass melting at 76—76·5°, and is probably a mixture of homologous alcohols containing 20 to 22 carbon atoms.

Ozokerite appears to represent an intermediate stage between the wax of algæ and petroleum, the products of distillation being of the same kind, although they are formed in different proportions. Ozokerite also contains small amounts of an ester hydrolysable by alcoholic potash.

Pyropissite, which has probably been formed from the remains of successive generations of algæ, contains 25 per cent. of wax and 23·4 per cent. of mineral residue, 72·9 per cent. of which is silica. In this case, a bed of the remains of algæ with siliceous skeletons has probably been covered by a second deposit of green algæ, which vegetated when the depth of water became less, and the whole has then been covered over by a mineral deposit. In the formation of petroleum, this wax would gradually lose methane and carbon dioxide and pass into ozokerite, which in its turn would yield petroleum. The sulphur of petroleum, as already mentioned, is probably to be ascribed to the activity of sulphur bacteria living contemporaneously with the algæ. A. H.

Action of Bromine on Methyltrimethylene in Absence of Light. By Nicolaus I. Demjanoff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 217—221).—The principal product of the action of bromine on methyltrimethylene in the dark is $\alpha\gamma$-dibromobutane, whilst smaller proportions of 1-bromo-1-methyltrimethylene and $\alpha\gamma\gamma$-tribromobutane are also formed. T. H. P.

Reduction of the Primary Dinitro-hydrocarbons with Aluminium Amalgam. By Giacomo Ponzio (*J. pr. Chem.*, 1902, [ii], **65**, 197—200).—It is shown that by the reduction of primary dinitro-hydrocarbons with aluminium amalgam, ammonia, and a primary amine, containing the same number of carbon atoms as the dinitro-compound, are obtained, an aldoxime being formed as an intermediate product. R. H. P.

Compounds of Alcohol with the Chlorides of Manganese and Cobalt. By F. Bourion (*Compt. rend.*, 1902, **134**, 555—557).—Anhydrous manganous chloride dissolves readily in absolute alcohol, forming a pale rose-coloured solution, which on evaporation deposits large, rose-coloured crystals, $MnCl_2,3EtOH$; this compound has a sp. gr. 1·35 at 20°/4°, and loses alcohol when exposed to the air, or over sulphuric acid in an exhausted desiccator; when heated at 200° in an atmosphere of carbon dioxide, it loses alcohol, but at a temperature approaching red heat, ethyl chloride is formed.

Cobalt chloride forms a *compound*, $2CoCl_2,5EtOH$, which crystallises in hygroscopic blue needles having a sp. gr. 1·32 at 22°/4°. Nickel chloride is but little soluble in alcohol. K. J. P. O.

Certain Reactions produced by the Aid of Magnesium Amalgam.

By Léon Meunier (*Compt. rend.*, 1902, **134**, 472—473).—Magnesium amalgam attacks cold alcohol, forming magnesium ethoxide and liberating a steady current of hydrogen which is capable of reducing the alkyl iodides to saturated hydrocarbons even more readily than the zinc-copper couple; benzene may with advantage be added to moderate the action. Magnesium ethoxide is a white powder, resembling the corresponding alkali derivatives, and on treatment with dry chlorine yields acetaldehyde, magnesium chloride, and hydrogen chloride.

Magnesium amalgam reacts energetically with acetaldehyde, the reduction being moderated by the addition of benzene or ether; the product, when boiled with alcohol and subsequently filtered, furnishes a solution from which $\beta\gamma$-butylene glycol (b. p. 185°) is isolated by fractional distillation. G. T. M.

Pyrogenic Contact-reactions of Organic Compounds. II and III.

By Wladimir N. Ipatieff (*Ber.*, 1902, **35**, 1047—1057, 1057—1064. Compare this vol., i, 4).—Iron exerts a catalytic action on the decomposition of alcohol into aldehyde and hydrogen; paraldehyde passed through an iron tube is converted chiefly into methane and carbon monoxide. The action of zinc oxide is very similar to that of metallic zinc.

When *iso*butyl alcohol is passed over heated zinc or brass, 60—70 per cent. is converted into the aldehyde, which can be advantageously prepared in this way. *iso*Amyl alcohol gave a complex mixture of unsaturated hydrocarbons. Allyl alcohol appears to give acraldehyde as a first product, but this is decomposed into carbon monoxide, propylene, and probably divinyl. Benzyl alcohol gave benzaldehyde, and also benzene and carbon monoxide.

Methyl alcohol is decomposed by heat into trioxymethylene, a decomposition which is facilitated by zinc, but iron causes a further decomposition into hydrogen and carbon monoxide. *iso*Propyl alcohol is decomposed by heat into propylene and acetone, but the latter is further decomposed into methane and carbon monoxide; in presence of brass, the action takes place at a lower temperature and acetone can be separated in considerable quantities.

In presence of graphite, the alcohols are decomposed almost exclusively into an olefine and water, aldehydes being only formed in small quantities. By this method, ethylene and propylene can readily be prepared, whilst *iso*amyl alcohol and *iso*butyl alcohol give mixtures of olefines. Methyl alcohol, under similar conditions, yields considerable quantities of methane. T. M. L.

Constitution of Dibutyl and Diœnanthyl [Diheptyl] Alcohols.

By Marcel Guerbet (*Compt. rend.*, 1902, **134**, 467—469. Compare Abstr., 1901, i, 182).—The partial oxidation of dibutyl alcohol gives rise to dibutyric acid, $C_8H_{16}O_2$, a result which shows that the alcohol is a primary one; the ultimate products of oxidation with chromic acid are valeric, butyric, and acetic acids and carbon dioxide; the production of these substances justifies the belief that dibutyl alcohol and dibutyric acid have the following formulæ,

$$C_4H_9{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH, \text{ and } C_4H_9{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H,$$

respectively.

Diœnanthyl (diheptyl) alcohol, on gentle oxidation, yields diœnanthoic acid, $C_{14}H_{28}O_2$, a substance which, on further treatment with chromic acid, gives rise to octoic, heptoic, valeric, butyric, and acetic acids and carbon dioxide; these results indicate that the alcohol and the corresponding acid have the formulæ

$$CH_2Me{\cdot}[CH_2]_2{\cdot}CH(C_7H_{15}){\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

and $CH_2Me{\cdot}[CH_2]_2{\cdot}CH(C_7H_{15}){\cdot}CH_2{\cdot}CO_2H$, respectively.

In the production of these alcohols, the coalescence of the two residues takes place at the β-carbon atom with respect to the carbinol group. G. T. M.

Synthesis of Tertiary Alcohols by means of Organo-magnesium Compounds. By Michael I. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 26—31).—The conditions to be observed in order to obtain good yields of tertiary alcohols by the method given by Grignard (Abstr., 1900, i, 382) are as follows: (1) All the materials employed (ketone, alkyl iodide, and magnesium) must be perfectly dry. (2) The three phases of the reaction must all be carried out at as low a temperature as possible, and the whole process may conveniently be completed in one vessel—a large flask. Besides unsaturated hydrocarbons, the secondary products of the reaction comprise secondary alcohols and haloid compounds of high boiling point. The following alcohols have been prepared by the author.

Dimethyl*iso*amylcarbinol (compare Grignard, Abstr., 1901, i, 679) boils at 155° under 745 mm. pressure, has a sp. gr. 0·8228 at 20°/0°, and n_D 1·42085 at 20°.

Methylethylbutylcarbinol, $CH_2Pr^{\alpha}{\cdot}CMeEt{\cdot}OH$, obtained from methyl butyl ketone, ethyl iodide, and magnesium, is a colourless liquid having the usual odour of tertiary alcohols and dissolving only slightly in water; it boils undecomposed at 158—160° under 745 mm. pressure, and does not solidify when cooled in a mixture of ice and salt; the sp. gr. at 19°/0° is 0·8273, and n_D 1·42735 at 19°.

Tripropylcarbinol, $CPr^{\alpha}_3{\cdot}OH$, obtained together with dipropylcarbinol from dipropyl ketone, propyl iodide, and magnesium, boils undecomposed at 193—195° under 737 mm. pressure, and has a sp. gr. 0·8338 at 21°/0°, and n_D 1·43557 at 21°. T. H. P.

Action of Dilute Acids on Glycols. By Adolf Lieben (*Monatsh.*, 1902, **23**, 60—75).—αβ-Glycols or the corresponding alkylene dichlorides and dibromides, on treatment with dilute acids or even on heating with water, yield aldehydes and ketones and no alkylene oxide; thus propylene glycol gives propaldehyde and acetone. αδ-and αε-Dihydric alcohols, for example, αδ-dihydroxypentane, αε-dihydroxypentane, αε-dihydroxyhexane, on treatment with dilute sulphuric acid, yield cyclic oxides; the corresponding alkylene dichlorides yield the same oxide. These oxides are reconverted into the alkylene dihaloids by the action of concentrated halogen acids.

The αγ-glycols break down in a complicated manner. The glycol from *iso*butaldehyde and formaldehyde, $CMe_2(CH_2\cdot OH)_2$, gives *iso*valeraldehyde, methyl *iso*propyl ketone and a double cyclic oxide, $C_{10}H_{20}O_2$, boiling at 180°. The glycol from acetaldehyde and propaldehyde, $OH\cdot CHMe\cdot CHMe\cdot CH_2\cdot OH$, gives methylethylacetaldehyde (?) and a double oxide, $C_{10}H_{20}O_2$, boiling at 180—185°. The glycol from *iso*butaldehyde, $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, gives a simple oxide, $C_8H_{16}O$, which boils at 120—122°, and a double oxide, $C_{16}H_{32}O_2$, boiling at 260—262°. The glycol from *iso*butaldehyde and *iso*valeraldehyde, $CHMe_2\cdot CH_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, yields a hydrocarbon, C_9H_{16}, a simple oxide, $C_9H_{18}O$, and a double oxide, $C_{18}H_{36}O_2$, which boils at 240°. The glycol from benzaldehyde and propaldehyde,

$$OH\cdot CHPh\cdot CHMe\cdot CH_2\cdot OH,$$

gives benzaldehyde and α-methylhydrocinnamaldehyde. The glycol from benzaldehyde and *iso*butaldehyde, $OH\cdot CHPh\cdot CMe_2\cdot CH_2\cdot OH$, gives a hydrocarbon, $CHPh{:}CMe_2$, which boils at 182—183°, and a formal, $CH_2{<}\begin{smallmatrix}O\cdot CHPh\\ O\text{—}CH_2\end{smallmatrix}{>}CMe_2$, which boils at 135° under 15 mm. pressure.

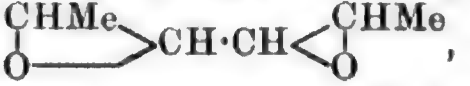
The mechanism of the reactions by which these various substances are formed from the glycols is discussed in the paper. K. J. P. O.

βε-Hexanediol and its Derivatives. By Paul Duden and R. Lemme (*Ber.*, 1902, **35**, 1335—1343).—*βε-Hexanediol*, obtained when acetonylacetone is reduced with sodium amalgam in the presence of carbon dioxide, is a colourless oil of the consistency of glycerol, boils at 216—218° under 750 mm. pressure, or at 120—122° under 12 mm. pressure, has a sp. gr. 0·9610 at 20°/4° and n_D 1·4475 at 20°; it forms a *diacetate*, which is a mobile liquid boiling at 230°, and when boiled with dilute sulphuric acid yields *dimethyltetrahydrofurfuran*, $C_6H_{12}O$, which is a mobile liquid having a characteristic odour and forms a crystalline *ferrocyanide* and *ferricyanide*.

The diol, when treated with hydrobromic acid, yields a mixture of the racemic and meso-forms of βε-dibromohexane (see Wislicenus, Abstr., 1901, i, 664). βδ-Hexadiene (Abstr., 1897, i, 262), when treated with bromine (1 mol.), yields *βε-dibromo-β-hexene*, which is a strongly refracting oil boiling at 94—96° under 12—14 mm. pressure; when heated with methylamine, this yields 1 : 2 : 5-trimethylpyrroline and dimethyldiaminohexene, and when oxidised by permanganate, dibromodihydroxyhexane and then bromopropionic acid.

Dimethyldiaminohexene, $C_8H_{18}N_2$, is a yellowish oil which boils at 175—176°, has a sp. gr. 0·8424 at 20°/4° and n_D 1·4556 at 20°, and forms a hygroscopic *hydrochloride* which crystallises in rosettes of rhombic tablets melting at 185—187°, a *platinichloride* which crystallises in tablets melting and decomposing at 215—217°, a *picrate* which crystallises in prisms decomposing at 218°, and a *phenylthiocarbamide* which crystallises in flat prisms and melts at 196°. *Dibromodihydroxyhexane*,

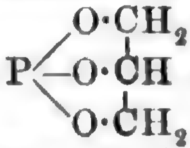
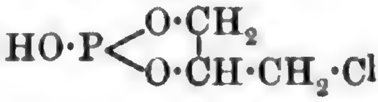
$C_6H_{12}O_2Br_2$, crystallises in tufts of prisms and when oxidised with permanganate yields bromopropionic acid. *Hexylene dioxide,*

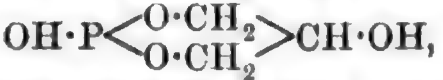


$$\begin{array}{c}\text{CHMe}\\ |\\ \text{O}\end{array}\!>\text{CH}\cdot\text{CH}<\!\begin{array}{c}\text{CHMe}\\ |\\ \text{O}\end{array},$$

obtained when dibromodihydroxyhexane is boiled with potassium carbonate solution, is a pale yellow, heavy oil which boils at 176—178°.

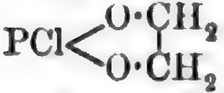
R. H. P.

Action of Phosphorus Trichloride on Glycerol and on Glycol. By P. Carré (*Bull. Soc. Chim.*, 1902, [iii], **27**, 264—269).—The author cannot confirm the formation of monoglycerophosphorous acid (compare this vol., i, 9) by the action of phosphorus trichloride on glycerol, and considers that the product of the reaction consists of the compounds  $P\begin{array}{l}\diagup\text{O}\cdot\text{CH}_2\\ -\text{O}\cdot\text{CH}\\ \diagdown\text{O}\cdot\text{CH}_2\end{array}$ and  $\text{HO}\cdot\text{P}<\!\begin{array}{l}\text{O}\cdot\text{CH}_2\\ \text{O}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{Cl}\end{array}$. On treatment with water, the former yields the substance

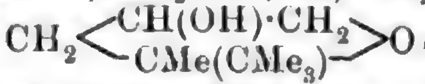
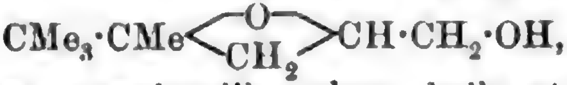
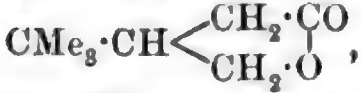


$$\text{OH}\cdot\text{P}<\!\begin{array}{l}\text{O}\cdot\text{CH}_2\\ \text{O}\cdot\text{CH}_2\end{array}\!>\text{CH}\cdot\text{OH},$$

which acts as a monobasic acid; the latter compound also gives rise to a monobasic acid, the study of which is not yet complete.

By the action of phosphorus trichloride on glycol, the compound  $\text{PCl}<\!\begin{array}{l}\text{O}\cdot\text{CH}_2\\ \text{O}\cdot\text{CH}_2\end{array}$ is formed, which on treatment with water yields the substance $OH\cdot P\colon O_2\colon C_2H_4$. The compound $OH\cdot PCl\cdot O\cdot CH_2\cdot CH_2Cl$ is probably also formed, but this has not yet been studied.

A. F.

Action of Sulphuric Acid on the [Substituted] Glycerol obtained from Methyl*tert.*butylallylcarbinol. By Alexander Petschnikoff (*J. pr. Chem.*, 1902, [ii], **65**, 168—187).—An attempt to determine the constitution of the "alcoholoxide," obtained by the action of sulphuric acid on dihydroxymethyl*tert.*butylallylcarbinol, $CMe_3\cdot CMe(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$. The "*alcoholoxide,*" $C_9H_{18}O_2$, probably  $\text{CH}_2<\!\begin{array}{l}\text{CH(OH)}\cdot\text{CH}_2\\ \text{CMe(CMe}_3)\end{array}\!>\text{O}$ or  $\text{CMe}_3\cdot\text{CMe}<\!\begin{array}{c}\text{O}\\ \text{CH}_2\end{array}\!>\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, is a viscous liquid, which has a faint, camphor-like odour, boils at 214—215° under 752 mm. pressure, and has a sp. gr. 0·9716 at 20°/20°. The molecular refraction shows that it is a saturated compound. It forms a *monoacetate*, has no reducing properties, and when oxidised by chromic acid yields a *lactone*, $C_8H_{18}O_2$, probably  $\text{CMe}_3\cdot\text{CH}<\!\begin{array}{l}\text{CH}_2\cdot\text{CO}\\ \text{CH}_2\cdot\text{O}\end{array}$, which crystallises in rhombic plates, melts at 96—98°, and can also be obtained by distilling β-methyl*tert.*-butylethylenelactic acid with sulphuric acid. The lactone, when boiled with barium hydroxide, yields the unstable *barium* salt of the corresponding acid, $(C_8H_{15}O_3)_2Ba$.

R. H. P.

History of the Electrolysis of Organic Acids. By Nikolaj A. Bunge (*Chem. Zeit.*, 1902, **26**, 217—218).—The author refers to the work done by Kolbe, Kekulé, Wurtz, and others before 1870, and recapitulates the results published by himself in 1870. According to his view, the products formed at the anode are not to be regarded as the result of a simple decomposition of the acid radicle, but are produced by the oxidation of the electrolyte by the oxygen separated at the anode. J. McC.

New Compounds of Methylene. By Marcel Descudé (*Compt. rend.*, 1902, **134**, 716—718. Compare Abstr., 1901, i, 644, and this vol., i, 149).—The chlorides of all monobasic acids, $R\cdot COCl$, react with trioxymethylene in the presence of zinc chloride (compare *loc. cit.*), producing the chloromethyl esters of the acid $R\cdot CO_2\cdot CH_2Cl$. From the chlorides of dibasic acids, no such esters were isolated, but the acid chlorides were converted into anhydrides. The chloromethyl esters react with potassium salts of acids above 160°, yielding methylene esters, $R\cdot CO_2\cdot CH_2Cl + R'\cdot CO_2K = KCl + R\cdot CO_2\cdot CH_2\cdot CO_2\cdot R'$. By these means there were prepared:

Chloromethyl valerate, boiling at 60° under 15 mm. pressure; *methylene divalerate*, boiling at 119° under 15 mm. pressure; *chloromethyl* o-*toluate*, boiling at 125° under 15 mm. pressure; *methylene di*-o-*toluate*, melting at 61—62°; *chloromethyl* m-*toluate*, boiling at 130—132° under 20 mm. pressure; *methylene di*-m-*toluate*, melting at 55—56° and boiling at 242—244° under 15 mm. pressure; *chloromethyl* p-*toluate*, boiling at 135—136° under 20 mm. pressure; *methylene di*-p-*toluate*, melting at 104°; *chloromethyl phenylacetate*, boiling at 138—140° under 15 mm. pressure; *methylene diphenylacetate*, boiling at 245—247° under 15 mm. pressure; *methylene acetate-benzoate*, $CH_3\cdot CO_2\cdot CH_2\cdot CO_2\cdot C_6H_5$, melting at 38° and boiling at 255—260°; *methylene phenylacetate-benzoate*, boiling at 230° under 12 mm. pressure; *methylene benzoate-o-toluate*, melting at 51—52°; *methylene benzoate*-m-*toluate*, melting at 36°, boiling at 227° under 12 mm. pressure, and *methylene benzoate*-p-*toluate*, melting at 74—75°; the last-mentioned substance was prepared from chloromethyl *p*-toluate and potassium benzoate, and from *chloromethyl benzoate* and (1) *p*-toluic acid or (2) potassium *p*-toluate.

All these substances crystallise in prismatic needles. On adding water to a solution of any of these esters in concentrated sulphuric acid, formaldehyde is evolved. K. J. P. O.

Mixed Glycerides in Animal Fat. By Willy Hansen (*Arch. Hygiene*, 1902, **42**, 1—15).—When repeatedly crystallised from ether, the stearin of beef and mutton yields a product melting at 62·5° which retains this melting point after recrystallisation from chloroform, benzene, and ether. This substance agrees in properties (saponification number, &c.) with a *distearopalmitin*, and on hydrolysis yields a mixture of acids melting at 64° which also agrees with the mixture obtainable from such a compound. When it is recrystallised from boiling amyl alcohol, it is converted into *tristearin* melting at 66·8°, and yielding pure stearic acid melting at 69·2°. This conversion of distearopalmitin into tristearin and either tripalmitin or dipalmitostearin by a reaction between several molecules of the fat, accounts for the so-called double melting point of stearin, which has been observed by many authors. The mixed glycerides obtained from stearin by these authors melt at about 55°, and at a higher temperature yield tristearin, which separates out and then redissolves at a still higher temperature, usually about 71°.

By a similar method, the following compounds have been isolated, the saponification and iodine numbers agreeing in all cases with those required by the constitution assigned: *dipalmitostearin*, melting at 55°; *dipalmito-olein*, melting at 48°; *stearopalmito-olein*, melting at 42°. *Tripalmitin*, melting at 52°, was also obtained, but it is possible that it was formed in a similar manner to tristearin and did not actually occur in the original fat. A. H.

Composition of Cocoa Butter. By J. Klimont (*Monatsh.*, 1902, **23**, 51—59).—This paper contains a more detailed account of work previously published (Abstr., 1901, i, 663). The glyceride, $C_{51}H_{96}O_6$ (m. p. 25—27°), is stated to be myristopalmito-olein; the saponification number is 211·7, and the iodine number 32·1.

K. J. P. O.

Unsaturated Acids with two Double Linkings. Homologues of Sorbic Acid. By Oscar Doebner [and, in part, A. Weissenborn] (*Ber.*, 1902, **35**, 1136—1147. Compare Abstr., 1900, i,536, and 1901, i, 578).—*β-Vinylacrylic acid*, $CH_2:CH\cdot CH:CH\cdot CO_2H$, was prepared by heating acraldehyde, malonic acid, and pyridine for 4 hours at 100°; carbon dioxide was evolved, and a yellowish, syrupy liquid obtained which was poured into dilute sulphuric acid. The acid may be extracted with ether and crystallises in long, colourless, very hygroscopic prisms and short rhombohedra melting at 80° to a mobile liquid, which becomes syrupy at 100—115°, giving methane (?) and liquid hydrocarbons. The alkali salts are very soluble and hygroscopic; the *silver* salt forms small needles; the *calcium* salt is a white, crystalline powder; the *zinc* and *barium* salts are readily soluble; the *lead* salt is a crystalline precipitate.

By the action of bromine, β-vinylacrylic acid is converted into *αβγδ-tetrabromovaleric acid*, $CH_2Br\cdot[CHBr]_3\cdot CO_2H$, which crystallises in rhombohedra melting at 160°.

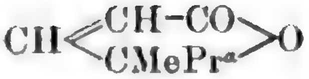
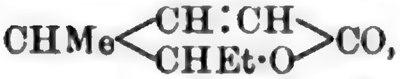
On reduction with sodium amalgam, allylacetic acid,

$$CH_2:CH\cdot[CH_2]_2\cdot CO_2H,$$

(b. p. 188°), is obtained, and not, as was expected, ethylidenepropionic acid. On oxidation with dilute permanganate, oxalic and racemic acids were formed. On keeping, β-vinylacrylic acid polymerises to an acid which decomposes at 300°.

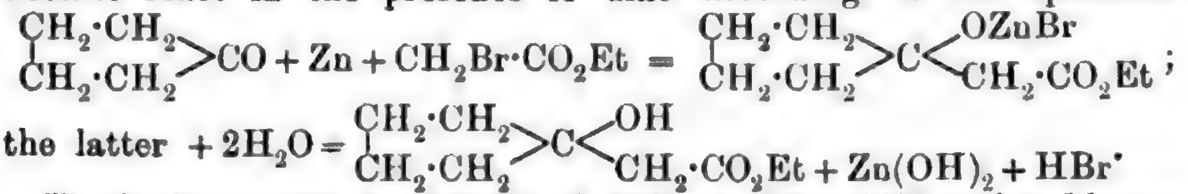
γ-Methylsorbic acid could only be obtained in small quantity from αβ-dimethylacraldehyde and malonic acid.

γε-Dimethylsorbic acid, $CH_2Me\cdot CH:CMe\cdot CH:CH\cdot CO_2H$, is formed from α-methyl-β-ethylacraldehyde and malonic acid, and is a golden-yellow, oily liquid boiling at 165° under 20 mm. pressure; the *silver* salt is a white, and the *copper* salt a pale green, precipitate; the *magnesium* salt is crystalline; a basic *aluminium* salt was obtained.

γε-Dimethyl-γ-(or *δ-*)*hydroxyhydrosorbolactone*,  $CH\!<\!\begin{matrix}CH{-}CO\\ CMePr^{a}\end{matrix}\!>\!O$ or  $CHMe\!<\!\begin{matrix}CH\colon CH\\ CHEt\cdot O\end{matrix}\!>\!CO$, is formed together with the acid just mentioned, and is a yellow, oily liquid distilling at 145—150° under 20 mm. pressure; the *silver* salt of the corresponding acid, $C_8H_{13}O_3Ag$, is a white powder.

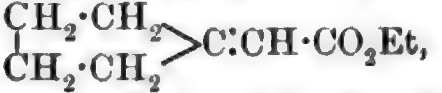
K. J. P. O.

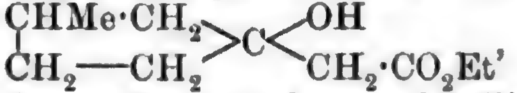
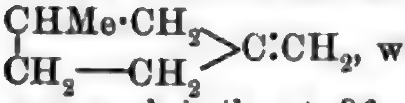
Condensation of Ethyl Bromoacetate with *cyclo*Pentanone and β-Methyl*cyclo*pentanone. By Nicolai A. Speransky (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 17—26).—*cyclo*Pentanone and ethyl bromoacetate react in the presence of zinc according to the equations:



$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!CO + Zn + CH_2Br\cdot CO_2Et = \begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}OZnBr\\ CH_2\cdot CO_2Et\end{matrix};$$

$$\text{the latter} + 2H_2O = \begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\ CH_2\cdot CO_2Et\end{matrix} + Zn(OH)_2 + HBr.$$

The hydroxy-ester thus obtained boils at 105—107° under 11 mm. pressure, but could not be prepared in a pure state. When heated with potassium hydrogen sulphate, it gives up water, yielding *ethyl* cyclo*pentanemethylidenecarboxylate*,  $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>\!C\colon CH\cdot CO_2Et$, which is a colourless, oily liquid having a pleasant odour and boiling at 82—84° under 11 mm. pressure. The free *acid*, $C_7H_{10}O_2$, which melts at 49—50° and boils at 122° under 11 mm. pressure, has a fatty-acid odour and dissolves in all the ordinary solvents excepting water. The *silver* salt was prepared and analysed. The *dibromide* of the acid, $C_7H_{10}O_2Br_2$, separates from dilute methyl alcohol in shining crystals melting at 88°. The *amide*, $C_6H_9\cdot CO\cdot NH_2$, crystallises from aqueous alcohol in transparent plates melting at 144°.

The condensation of ethyl bromoacetate with β-methyl*cyclo*pentanone is similar to that with *cyclo*pentanone and yields *ethyl β-methyl*cyclo*pentanolacetate*,  $\begin{matrix}CHMe\cdot CH_2\\ CH_2{-}{-}CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\ CH_2\cdot CO_2Et\end{matrix}$, as a pale yellowish-green liquid, having a pleasant odour and boiling at 113—115° under 11 mm. pressure; the corresponding *methyl* ester boils at 85—90° under 20 mm. pressure. When heated with potassium hydrogen sulphate, the ethyl ester gives up water and forms the ethyl derivative of an unsaturated acid, $C_{10}H_{16}O_2$, which is a colourless, oily liquid boiling at 90—92° under 11 mm. pressure. The corresponding *β-methyl*cyclo*pentanemethylidenecarboxylic acid*, $C_8H_{12}O_2$, boils at 128° under 11 mm. pressure and at 240° with decomposition under the ordinary pressure. The *silver* salt was prepared and analysed. When heated to a high temperature in a sealed tube, the ammonium salt of this acid yields, besides the amide and nitrile of the acid, *γ-methyl-α-methylene*cyclo*pentane*,  $\begin{matrix}CHMe\cdot CH_2\\ CH_2{-}{-}CH_2\end{matrix}\!>\!C\colon CH_2$, which has the characteristic odour of the naphthenes and boils at 96—97° under the ordinary pressure; its sp. gr. is 0·7750 at 16°. When oxidised with potassium permanganate, it gives β-methyl*cyclo*pentanone.

The *amide* of β-methyl*cyclo*pentanemethylidenecarboxylic acid,

$C_8H_{11}O{\cdot}NH_2$, forms plates melting at 126°. The *nitrile*, $C_7H_{11}{\cdot}CN$, is a liquid boiling at 208—210° under the ordinary pressure; on reduction, it yields an *amine*, $C_8H_{15}{\cdot}NH_2$, the *oxalate* of which was prepared and analysed. When treated with nitrous acid, the amine gives an *alcohol*, $C_8H_{15}{\cdot}OH$, boiling at 180°. T. H. P.

Aliphatic and Cyclic Ethyl Citralideneacetoacetates. HAARMANN and REIMER (D.R.-P. 124227 and 124228).—Aliphatic *ethyl citralideneacetoacetate* (*ethyl ψ-iononecarboxylate*), $C_{16}H_{24}O_3$, prepared by heating on the water-bath a mixture of citral, glacial acetic acid, ethyl acetate, and acetic anhydride, is separated by fractional distillation in a current of steam, the ester being the least volatile product of reaction.

Ethyl cyclo*citralideneacetoacetate* (*ethyl iononecarboxylate*) melts at 49°, boils at 215° under 100 mm. and at 160° under 11 mm. pressure, and has a sp. gr. 1·0387 at 19° and n_D 1·5110; it is produced either by distilling the aliphatic ester in a vacuum or by treating it with concentrated sulphuric acid.

β-Iononecarboxylic acid, $C_{14}H_{20}O_3$, obtained together with β-ionone by the hydrolysis of the aliphatic ester, melts at 208°, and when heated above this temperature evolves carbon dioxide, forming β-ionone; it is sparingly soluble in alcohol, ether, or benzene. G. T. M.

Constitution of Tariric Acid. By ALBERT ARNAUD (*Compt. rend.*, 1902, **134**, 473—475).—Tariric acid, extracted from the glucoside of the seed of a *tariri* growing in Guatemala, is an isomeride of stearolic acid and has the constitution indicated by the formula

$$CH_3{\cdot}[CH_2]_{10}{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}CO_2H;$$

when reduced with hydriodic acid and red phosphorus at 210°, it furnishes stearic acid, whilst its oxidation with potassium permanganate solution or nitric acid leads to the production of adipic and lauric acids. The attack of the oxidising agents is directed towards the unsaturated linking between the fifth and sixth carbon atoms, counting from the carboxyl group (compare Abstr., 1892, 582; 1896, i, 522). G. T. M.

Halogen Derivatives of Malonic Acid. By RICHARD WILLSTÄTTER (*Ber.*, 1902, **35**, 1374—1378).—Dibromomalonic acid was prepared by exposing to sunlight a solution of malonic acid and bromine in formic acid of sp. gr. 1·2; a vigorous reaction took place and a yield of 90—100 per cent. of the acid was obtained; it crystallises in prisms or needles which melt and decompose at 130—131° and are unchanged in the air. When warmed with water, this acid is quickly converted into dibromoacetic acid (compare Petrieff, Abstr., 1874, 787, and 1878, 490, and Massol, *Ann. Chim. Phys.*, 1894, [vii], 1, 200); the *ammonium* salt forms prisms or plates. *Methyl dibromomalonate*, prepared by brominating methyl malonate, crystallises in lustrous needles or leaflets melting at 63—65°. *Di-iodomalonic acid* is readily obtained by heating malonic acid with iodine and iodic acid in formic acid solution (compare Angeli, Abstr., 1893, i, 307), and is very unstable, decomposing in aqueous solution into iodoacetic acids and giving up iodine to organic solvents; it crystallises from formic acid in lustrous, pale yellow leaflets melting and decomposing at 119—120°; the *methyl ester* was prepared by the action of potassium iodide on an alcoholic solution of methyl dibromomalonate and crystallised in pale yellow needles melting at 79—80°. K. J. P. O.

Synthesis of Dimethylsuccinic Acid in Sunlight. By WLADIMIR ZERNOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 140—142).—When ethyl α-iodopropionate, diluted with alcohol, is sealed up in a tube with mercury and shaken in presence of air, an action immediately begins to take place resulting in the formation of diethyl dimethylsuccinate: $2CHMeI{\cdot}CO_2Et = CO_2Et{\cdot}CHMe{\cdot}CHMe{\cdot}CO_2Et + I_2$. Small quantities of products of higher boiling point are also obtained, these being due to the oxidation of the residue of the ethyl iodopropionate left after the removal of the iodine. T. H. P.

Dioxytariric and Ketotariric Acid. By ALBERT ARNAUD (*Compt. rend.*, 1902, **134**, 547—549. Compare Abstr., 1892, i, 582).—*Dioxytariric acid*, $CH_3{\cdot}[CH_2]_{10}{\cdot}CO{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO_2H$, is obtained when tariric acid is oxidised with potassium permanganate or fuming nitric acid; it crystallises in yellow plates melting at 98°; the *dioxime* crystallises in small, colourless needles melting at 166—167°.

When dissolved in concentrated sulphuric acid, tariric acid is converted into *ketotariric acid*, $CH_3{\cdot}[CH_2]_{10}{\cdot}CO{\cdot}[CH_2]_5{\cdot}CO_2H$, which crystallises in pearly leaflets melting at 75°; it forms an insoluble acid *ammonium* salt and an oily *oxime*. K. J. P. O.

Synthesis of Muconic Acid from Glyoxal and Malonic Acid. By OSCAR DOEBNER (*Ber.*, 1902, **35**, 1147—1148. Compare Abstr., 1901, i, 188).—Glyoxal (1 mol.) and malonic acid (3 mols.) were heated with pyridine for 3—4 hours on the water-bath. The product was poured into dilute sulphuric acid and the solution extracted with ether. The muconic acid thus obtained crystallised from water in colourless needles melting and decomposing at 292° (compare Baeyer and Rupe, Abstr., 1890, i, 875). For the purpose of identification, it was converted into the silver salt and the dimethyl ester (m. p. 158°). K. J. P. O.

Existence of Racemic Compounds in Solution. By GIUSEPPE BRUNI and M. PADOA (*Atti R. Accad. Lincei*, 1902, **11**, i, 212—217).—With the view of obtaining evidence as to the existence of racemic compounds in a dissolved state, the authors have studied the cryoscopic behaviour of the dimethyl esters of diacetyltartaric and diacetylracemic acids in solution in benzene, *p*-xylene, ethylene bromide, and bromoform. For low concentrations, both the active and racemic esters give the normal molecular weights in solution, whilst with increasing concentrations more or less association takes place with the different solvents. When a solution of the diacetyltartrate is taken as the solvent, the depressions of freezing point caused by the addition of increasing quantities of the racemic compound indicate values for the molecular weight of the latter considerably greater than those obtained for solutions of similar concentration, but containing only the racemic form. Hence it would seem that in presence of excess of an active compound, the corresponding racemic compound can exist as such in solution. T. H. P.

Formaldehyde. By PAUL N. RAIKOW (*Chem. Zeit.*, 1902, **26**, 135).—When anhydrous potassium carbonate is added to a 40 per cent. aqueous solution of formaldehyde, the solution becomes blue, and on further addition of the solid it becomes yellowish. When the solution is saturated with the carbonate, separation takes place into two clear liquid layers, the upper of which consists of formaldehyde (probably a mixture of different modifications). This liquid has a sp. gr. 1·1902 at 16°, is quite mobile and completely miscible with water, alcohol, or ether, and can be distilled without decomposition. After the main portion has passed over at about 91°, a fraction volatilises at 110° to 112° which condenses to a colourless, gelatinous, voluminous solid. If a perfectly anhydrous liquid be subjected to distillation, this solidification does not take place. The investigation of these modifications of formaldehyde is being continued. J. McC.

Physico-chemical Properties of Chloral Hydrate and its Employment in Pharmaceutical Chemistry. By RICHARD MAUCH (*Arch. Pharm.*, 1902, **240**, 113—134).—At 17·5°, 1 part of water dissolves 4·74 parts of chloral hydrate, and 1 part of absolute alcohol 4·4 of chloral alcoholate. Aqueous solutions were prepared containing 80, 60, and 30 per cent. of chloral hydrate, and a 60 per cent. solution of chloral alcoholate in absolute alcohol; a study was made of the solvent action of these solutions, more particularly of the first two, upon representatives of various classes of organic compounds. Fuller details of these solubilities are given elsewhere (*Inaug. Diss.*, Strassburg, 1898). As a rule, alkaloids dissolve readily in these solutions; so do resins, balsams, and gums; also colouring matters; several proteids, but not silk; several carbohydrates, but not cellulose, whilst starch rather swells up than dissolves. Essential oils dissolve when they do not contain terpenes, not if they do; oils are but little soluble, the drying oils more so than the others; fats and waxes are generally insoluble, and so are hydrocarbons, indiarubber, and guttapercha. Inorganic substances are little soluble; 1 part of iodine dissolves in 560 of the 80 per cent. solution.

Substances that bring about liquefaction when mixed with chloral hydrate dissolve readily in a concentrated aqueous solution of the latter, and *vice versâ*. Substances are also soluble which produce liquefaction when warmed with chloral hydrate; they are the more soluble the lower the temperature of liquefaction lies below the melting point of chloral hydrate. C. F. B.

[Heptaldehyde and its Homologues.] SCHIMMEL & Co. (D.R.-P. 126736).—Heptaldehyde boils at 44·4° and 154° under 9 and 747 mm. pressure respectively; it has a sp. gr. 0·8231 at 150°.

n-Octaldehyde boils at 60—63° under 10 mm., and at 72° under 20 mm., pressure; it has a sp. gr. 0·827 at 15° and n_D 1·41667; its naphthacinchoninic acid melts at 234°.

n-Nonaldehyde boils at 80—82° under 13 mm. pressure and has a sp. gr. 0·8277 at 15° and n_D 1·42452; its naphthacinchoninic acid melts at 234°.

n-Decaldehyde boils at 97—98° under 15 mm., and at 207—209° under 755 mm., pressure; it has a sp. gr. 0·828 at 15° and n_D 1·4273; its naphthacinchoninic acid melts at 237°.

These aldehydes were prepared by distilling mixtures of barium formate with the barium salt of the corresponding acid in a vacuum.

G. T. M.

Succindialdehyde. II. By CARL D. HARRIES (*Ber.*, 1902, **35**, 1183—1189. See Abstr., 1901, i, 451).—A detailed description of five polymeric modifications of succindialdehyde. A liquid modification is obtained when the dialdehyde is distilled under 10 mm. pressure; from a cryoscopic determination in benzene, it appears to be a termolecular modification. The glassy modification previously described (*loc. cit.*), when heated at about 30° under 0·25 mm. pressure, is quinquemolecular, and termolecular when heated to about 55°; these different modifications of the glassy aldehyde show the same chemical behaviour, but determinations of the molecular refraction indicate that at about 65° the quinquemolecular modification becomes unimolecular. A solid modification, which is crystalline and melts at 64°, is obtained when the molten glassy form at 50° is immersed in water at the same temperature. Another crystalline modification is obtained by the spontaneous evaporation of a benzene solution of the aldehyde; it crystallises in needles and melts at 130—140°. An amorphous form is obtained by the evaporation of an acetone solution containing anhydrous oxalic acid; this is a white powder which partly passes into the simpler modifications at 90—100°.

Succintetraethylacetal boils at 137° under 35 mm. pressure, or at 116° under 20 mm. pressure. The dialdehyde, when reduced, yields tetramethylene glycol (butane-1 : 4-diol).

R. H. P.

New Proof of the Constitution of the Synthetical Methylheptenone. By CARL D. HARRIES (*Ber.*, 1902, **35**, 1179—1183).—Methylheptenone, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, when oxidised with permanganate, yields *dihydroxymethylheptanone*,

$$OH{\cdot}CMe_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}COMe,$$

which crystallises in star-shaped clusters of prisms, melts at 66—67°, and boils at 134—136° under 11 mm. pressure. When the oxidation is continued either with chromic acid or permanganate, the *hydroxy-diketone*, $OH{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, is obtained; this, which can also be obtained directly by the oxidation of methylheptenone by permanganate in acetone solution, is a colourless oil boiling at 126—127° under 15 mm. pressure and yielding a *disemicarbazone* which melts and decomposes at 226°, and a *dioxime* which crystallises in transparent prisms, sinters at 119°, and melts at 123°. The glycol, when heated with 5 per cent. sulphuric acid, yields αα-dimethylacetonylacetone. The formula $CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}COMe$ for methylheptenone is therefore to be discarded.

R. H. P.

Derivatives of Methyl Nonyl Ketone. By HENRI CARETTE (*Compt. rend.*, 1902, **134**, 477—479. Compare Abstr., 1901, i, 367).—Methyl nonyl ketone and hydrogen cyanide slowly combine in the presence of a few drops of concentrated ammonia solution, giving rise to the *cyanohydrin*, $C_9H_{19}\cdot CMe(OH)\cdot CN$, a colourless oil which is decomposed even when distilled under reduced pressure. This substance, when heated on the water-bath for 1 hour with concentrated hydrochloric acid, is partially hydrolysed, yielding the *amide*,

$$C_9H_{19}\cdot CMe(OH)\cdot CO\cdot NH_2,$$

a compound crystallising in nacreous lamellæ and melting at 86—87°.

The *acid*, $C_9H_{19}\cdot CMe(OH)\cdot CO_2H$, is obtained when the amide or the cyanohydrin is heated for a longer time with excess of concentrated hydrochloric acid; it separates in nacreous crystals melting at 46°. The acid is insoluble in water, but dissolves in the ordinary organic solvents; its ammonium and alkali salts are soluble, and separate from their solutions in nacreous crystals. An *acidic* compound containing nitrogen, also produced during the hydrolysis of the cyanohydrin, forms crystalline lamellæ melting at 185°; its constitution is probably that indicated by the formula $C_9H_{19}\cdot CMe(NH_2)\cdot CO_2H$.

G. T. M.

Derivatives of Arabinose. By G. CHAVANNE (*Compt. rend.*, 1902, **134**, 661—663. Compare Koenigs and Knorr, Abstr., 1901, i, 588, and Fischer and Armstrong, Abstr., 1902, i, 257, 671).—*Bromotriacetylarabinose*, $C_5H_6OBr(OAc)_3$, prepared by mixing arabinose and acetyl bromide together at low temperatures, crystallises in hard, transparent, colourless needles melting at 137°; it is sparingly soluble in light petroleum or methyl and ethyl alcohols, but readily dissolves in ether, acetic acid, chloroform, or benzene in the presence of water; the compound decomposes slowly at the ordinary temperature, more rapidly on heating; it has $[\alpha]_D$ −283°50′, and reduces warm Fehling's solution.

Chlorotriacetylarabinose, $C_5H_6OCl(OAc)_3$, produced from acetyl chloride and arabinose at the ordinary temperature, is extracted from the syrupy product by chloroform and precipitated from its solution in this solvent by ether; it is thus obtained as a crystalline powder having $[\alpha]_D$ −224°49′, melting at 148—149°, and reducing warm Fehling's solution. The substance resembles its bromine analogue in solubility and is similarly decomposed by water. These two compounds, when heated with silver acetate in acetic acid solution, yield a *compound* crystallising in long needles and melting at 80°. *Arabinose phenylhydrazone*, obtained by mixing phenylhydrazine with arabinose dissolved in dilute alcohol, crystallises in white needles melting at 150—151°; it is very sparingly soluble in water. G. T. M.

***d*-Arabinose and *d*-Arabonic Acid and the Estimation of Arabinose.** By CARL NEUBERG and JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1902, **35**, 31—40).—*l*-Arabinose can be readily prepared from cherry gum. Synthetical processes have to be adopted in order to prepare *d*- and *r*-arabinose in quantity. For the preparation of *d*-arabinose, Wohl's method was found to be the best, namely, from *d*-glucosoxime, through the stages of *d*-penta-acetylgluconontrile and *d*-arabinosediphenylhydrazone.

d-Arabonic acid is most readily made from its diacetamide compound, obtained by treating *d*-penta-acetylgluconontrile, first with ammoniacal silver oxide, then with ammonium sulphide, and finally, at 100°, with fuming hydrobromic acid.

A method of estimating arabinose in urine is described which consists in weighing the hydrazone obtained by adding diphenylhydrazine to the wine, after acidification with acetic acid, evaporation and precipitation of the urates and inorganic salts by addition of hot 96 per cent. alcohol. W. D. H.

Glucophosphoric Acid. By P. A. LEVENE (*J. Amer. Chem. Soc.*, 1902, **24**, 190—191).—The author has reinvestigated a crystalline substance obtained by Palladin from various seeds (*Zeit. Biol.*, 1894, **31**, 199). A copper salt prepared from it contains: C, 16·95; H, 2·85; N, 2·41; P_2O_5, 24·10; CuO, 35·66; ash, 57·67 per cent. On hydrolysis with dilute mineral acids, it yields phosphoric acid and a substance which reduces Fehling's solution and gives a crystalline product with phenylhydrazine. E. G.

Hepta-acetylchloromaltose. By RICHARD FOERG (*Monatsh.*, 1902, **23**, 44—50).—*Hepta-acetylchloromaltose*, $C_{12}H_{14}O_3Cl(OAc)_7$, was prepared by saturating maltose suspended in acetic anhydride at −21° with hydrogen chloride; it crystallises in large, rhombic leaflets melting at 118—120°, and has $[\alpha]_D$ −159° at 20° in chloroform solution. The substance is not identical with the isomeride obtained from octoacetylmaltose by Fischer and Armstrong (Abstr., 1901, i, 671) which melts at 64—66°.

Hepta-acetylmethylmaltoside, obtained when the preceding compound is shaken with methyl alcohol and silver carbonate, crystallises in leaflets melting at 125—127°. *Hepta-acetylethylmaltoside* forms elongated leaflets or needles which change at 118° and melt at 121—123°.

K. J. P. O.

Melibiose. By ARMINIUS BAU (*Chem. Zeit.*, 1902, **26**, 69—70. Compare Abstr., 1896, i, 453; 1900, i, 77).—The melibiose was prepared from melitriose by boiling with 2—3 per cent. acetic acid solution. When crystallised from water, it contains 2 mols. of water of crystallisation. The rotation of the solution increases on standing, and the final value is $[\alpha]_D$ +129·641° at 20° (for anhydrous melibiose $[\alpha]_D$ would be +143·27° at 20°); with increase of concentration, the specific rotation increases slightly.

Melibiosazone melts at about 177—179° and decomposes with evolution of gas at about 180°, but these temperatures vary with the previous treatment of the substance. When heated at 95—100°, melibiosazone loses weight slowly, but not a constant amount. Digestion with water at 100° also causes decomposition.

Melibiose can best be recognised by a fermentation process. It is easily and completely fermented by bottom yeast (*Saccharomyces cerevisiæ*), but is not attacked by top yeast. J. McC.

Hepta-acetychlorolactose. By ALBERT BODART (*Monatsh.*, 1902, **23**, 1—8).—On treating lactose with acetic anhydride and concentrated sulphuric acid, an oil was obtained which distilled at 218—225° under 9 mm. pressure; from it petroleum extracts penta-acetyldextrose (m. p. 111·5°). When a suspension of lactose in acetic anhydride is saturated with hydrogen chloride at −20°, *hepta-acetylchlorolactose*,

$$C_{12}H_{14}O_8Cl(OAc)_7,$$

is obtained; it crystallises from a mixture of benzene and petroleum in colourless needles or prisms sintering at 117·5° and melting at 119—121°, and has $[\alpha]_D$ +71·75° at 20° in chloroform solution; acetylphenylhydrazine was the only product of the action of phenylhydrazine. On treating heptaacetylchlorolactose with silver acetate, octoacetyllactose, $C_{12}H_{14}O_3(OAc)_8$, is obtained, crystallising in plates or needles melting at 86°. K. J. P. O.

Decomposition of Carbohydrates by Ferments and Enzymes of Animal and Vegetable Origin. By WALTHER NIC. CLEMM (*Pflüger's Archiv*, 1902, **89**, 517—526).—The effect of various enzymes was tried on starch and glycogen. The resulting sugars were identified by the melting point and solubility of the osazones. Both potato starch and glycogen yield dextrose on treatment with filtered saliva. Dextrose is also formed when the liver of the pig and of the dog containing a large amount of glycogen is kept at 40° for 2 days in presence of thymol. On the other hand, both potato starch and glycogen are converted by malt extract into maltose. Pancreatin, prepared by the addition of alcohol to the pancreatic secretion of a dog, when digested with potato starch yields a sugar the osazone of which agrees in melting point with that of galactose. The secretion employed in this case had undergone slight putrefaction.

The glycerol extract of the pancreas of the pig, on the other hand, converts starch into a sugar, of which the osazone melts at 207—208°, but which does not appear to be identical with dextrose. A. H.

Diaminosulphonal. By ALBERT MANASSE (*Ber.*, 1902, **35**, 1372—1374).—On oxidising the phthaliminoethylmercaptole of acetone $(C_8H_4O_2{:}N{\cdot}C_2H_4{\cdot}S)_2CMe_2$, with potassium permanganate in acetic acid solution, *diphthaliminosulphonal*, $(C_8H_4O_2{:}N{\cdot}C_2H_4{\cdot}SO_2)_2CMe_2$, is produced, and crystallises in quadratic leaflets. *Diaminosulphonal hydrochloride*, $(NH_2{\cdot}C_2H_4{\cdot}SO_2)_2CMe_2,2HCl$, is formed, when the substance last mentioned is heated with hydrochloric acid under pressure at 150°; it decomposes at 227—233°; the *platinichloride* forms needles decomposing at 248—250°, the *aurichloride*, rhombic leaflets decomposing at 223—224°. *Diaminosulphonal*, obtained from the hydrochloride, crystallises in needles melting at 84—86°, absorbs carbon dioxide from the air, and forms a strongly alkaline aqueous solution; the *diacetyl* derivative crystallises in prisms melting at 165°.

K. J. P. O.

[Compounds of Ethylenediamine and its Derivatives with Mercuric Salts.] CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 125095).—*Ethylenediamine mercuricitrate*, produced by mixing together ethylenediamine and mercuric citrate in absolute alcohol, crystallises in white needles sintering at 110° and melting at 137°; it is readily soluble in water, yielding a strongly alkaline solution. The *mercurichloride* obtained by mixing its generators in aqueous solution forms white needles insoluble in water and alcohol, but dissolving in an aqueous solution of ethylenediamine; it darkens at 180° and decomposes at 225°. The *mercurisulphate* separates in white needles and is soluble in water, but not in alcohol; it darkens at 180° and decomposes at 210°. The corresponding *mercuricyanide* and *mercuribenzoate* melt at 144—145° and 107—108°, and crystallise in white needles and lustrous leaflets respectively. The *mercuri-acetate*, *-salicylate*, and *-nitrate* are obtained in a similar manner.

Diethylethylenediamine mercurinitrate and the corresponding *mercurisulphate*, *-chloride*, *-cyanide*, *-succinate*, and *-salicylate* melt respectively at 148—151°, 124—125°, 159—160°, 108—110°, 128—130°, and 181—183°.

Piperazine mercuri-acetate, obtained by treating mercuric acetate with piperazine in alcoholic solution, is moderately soluble in water; it darkens at 188° and melts at 198°.

These double salts may also be prepared by treating the mercuric salts with the carbonates of the organic amines. They have antiseptic properties and do not coagulate albumin. G. T. M.

The Oxime of Diacetoneamine; $\beta\gamma$-Diamino-β-methylpentane.

By MORIZ KOHN (*Monatsh.*, 1902, **23**, 9—21. Compare Abstr., 1901, i, 194, 367).—Diacetoneamino-oxime has a feeble reducing action on Fehling's solution, gives with copper sulphate a deep blue coloration, and a silver mirror with silver nitrate; with excess of mercuric chloride, a precipitate is formed which is soluble in hot water; the *sulphate*, $2C_6H_{14}ON_2,H_2SO_4$, crystallises in needles decomposing at 210—220°; the oxalate, $2C_6H_{14}ON_2,H_2C_2O_4$, in needles decomposing at 214°.

$\beta\gamma$-Diamino-β-methylpentane ($\beta\gamma$-diamino*iso*butane),

$$NH_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot NH_2,$$

is prepared by reduction of a solution of the amino-oxime in dilute acetic acid by sodium amalgam; it forms a mobile, ammoniacal liquid boiling at 147—155° and absorbs carbon dioxide from the air, forming a carbamate; the *hydrochloride* and *platinichloride* were prepared. The *compound* of the former, with mercuric chloride, $C_6H_{16}N_2,2HCl,3HgCl_2$, crystallises in needles melting at 181—183°.

The *dicarbamide*, $NH_2\cdot CO\cdot NH\cdot CMe_2\cdot CH_2\cdot CHMe\cdot NH\cdot CO\cdot NH_2$, prepared from the hydrochloride and silver cyanate, is a pale yellow solid; the *nitrate* crystallises in needles decomposing at 138—140°.

K. J. P. O.

Derivatives of Diaminoacetic Acid and Diaminomalonic Acid.

By RICHARD WILLSTÄTTER (*Ber.*, 1902, **35**, 1378—1387).—*Methyl tetramethyldiaminoacetate*, $CH(NMe_2)_2\cdot CO_2Me$, obtained by the interaction of methyl di-iodoacetate and excess of dimethylamine in solution in dry benzene, is a mobile, colourless oil, with an odour of formaldehyde, boiling at 57—58° under 12·5 mm. pressure; it is readily soluble in most solvents, immediately reduces silver nitrate and acidified permanganate solutions, gives no insoluble picrate, platinichloride, or aurichloride, is not attacked by cold aqueous alkali carbonates, but is decomposed by boiling aqueous alkali carbonates or by alkali hydroxides; with concentrated platinic chloride, dimethylamine is immediately eliminated. Methyl dibromoacetate and dimethylamine react in a different manner, yielding *dibromoacetyldimethylamide*, $CHBr_2·CO·NMe_2$, which crystallises in prisms, melts at 79—80°, and boils at 128° under 12 mm. pressure; with excess of dimethylamine, *hydroxydimethylaminoacetyldimethylamide*, $OH·CH(NMe_2)·CO·NMe_2$, is formed as a colourless oil boiling at 80° under 12 mm. pressure, and is soluble in all solvents; it is volatile with steam, reduces silver nitrate, and is immediately decomposed by alkalis and acids; with concentrated platinic chloride, half the dimethylamine is immediately eliminated.

Methyl tetramethyldiaminomalonate, $C(NMe_2)_2(CO_2Me)_2$, is prepared by the action of dimethylamine on methyl dibromomalonate in benzene solution at a low temperature; it crystallises from ether in rhombic plates, melts at 83—85°, is volatile with steam, and boils without decomposing; it is immediately decomposed by alkalis and acids and by methyl iodide. When hydrolysed by prolonged boiling with water, the dimethylamine salt of mesoxalic acid is obtained together with *tetramethyldiaminomalonic acid*, $C(NMe_2)_2(CO_2H)_2$, which was separated from the salt by recrystallisation from absolute alcohol; it forms a crystalline powder melting and decomposing at 133°, and immediately reduces silver nitrate; concentrated platinic chloride effects the elimination of the whole of the dimethylamine.

K. J. P. O.

Derivatives of Glycine, Alanine, and Leucine. By EMIL FISCHER (*Ber.*, 1902, **35**, 1095—1106. Compare Abstr., 1901, i, 675). —The substance formerly described as carbaminoglycylglycine ethyl ester is really *ethyl glycylglycinamidecarboxylate*,

$$CO_2Et·NH·CH_2·CO·NH·CH_2·CO·NH_2,$$

as it is not identical with the *carbaminoglycylglycine ethyl ester*, $NH_2·CO·NH·CH_2·CO·NH·CH_2·CO_2Et$, crystallising in slender needles and melting at 163° (165° corr.), which is obtained by the action of potassium cyanate on glycylglycine ethyl ester hydrochloride.

When diethyl glycylglycinecarboxylate is hydrolysed with 1 mol. of aqueous sodium hydroxide at the ordinary temperature, it is probable that carboxyethyl group first attacked is the same as that affected by ammonia; the product, *ethyl hydrogen glycylglycinecarboxylate*,

$$CO_2Et·NH·CH_2·CO·NH·CH_2·CO_2H,$$

crystallises from water or alcohol in small, flexible needles, melts at 140° (corr.), decomposes at 200°, and yields crystalline *copper* and *silver* salts. If 2 mols. of alkali are used in the hydrolysis and the liquid is boiled and subsequently acidified with hydrochloric acid, *glycylglycinecarboxylic acid*, $CO_2H·NH·CH_2·CO·NH·CH_2·CO_2H$, is obtained; it crystallises from water in stellate aggregates of needles, melts and decomposes at 208° (corr.), and yields a granular *silver* salt.

Glycylglycinamidecarboxylic acid,

$$CO_2H·NH·CH_2·CO·NH·CH_2·CO·NH_2,$$

obtained by hydrolysing its ester (ethyl glycylglycinamidecarboxylate) with 1 mol. of aqueous sodium hydroxide at the ordinary temperature, crystallises from warm water in small, colourless leaflets or prisms and melts and decomposes at 195° (corr.).

The action of guanidine on diethyl glycylglycinecarboxylate gives the *guanidine* salt, $C_6H_{11}O_4N_3$, of an *acid*, $C_5H_6O_4N_2$, which can be considered as the anhydride of glycylglycinecarboxylic acid; the salt crystallises from methyl alcohol in short, colourless prisms and melts at 224°.

Diethyl glycylglycyl-leucinecarboxylate,

$$CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO_2Et,$$

obtained by heating diethyl glycylglycinecarboxylate with leucine ethyl ester for 36 hours at 130—135°, crystallises from water in colourless prisms and melts at 109·5° (corr.).

Glycylglycine ethyl ester, when acetylated, yields the *acetyl* derivative, $NHAc\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, which crystallises from alcohol and melts at 152°; when its hydrochloride is shaken in aqueous solution with carbonyl chloride dissolved in toluene, it gives *carbonyldiglycylglycine ethyl ester*, $CO(NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et)_2$, which crystallises from water and melts and decomposes at 233° (corr.). *Carbonyldiglycylglycine*, $CO(NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H)_2$, obtained by hydrolysing the ester, crystallises from water and melts and decomposes at 232° (corr.); *carbonyldiglycylglycinamide*,

$$CO(NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2)_2,$$

crystallises from water in sheaves of needles melting and decomposing at 270°.

The product of the action of either ethyl or methyl alcohol and hydrogen chloride on alanine anhydride is a syrup which cannot be made to crystallise; that obtained by using ethyl alcohol readily interacts, however, with ethyl chlorocarbonate to form *diethyl alanylalaninecarboxylate*, $CO_2Et\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot CHMe\cdot CO_2Et$, which crystallises from ether, on adding light petroleum, in colourless needles melting at 70° (corr.).

Leucylleucine, $NH_2\cdot CH(C_4H_9)\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO_2H$, obtained by heating at 100° leucine anhydride (leucinimide) with hydrobromic acid saturated at 0°, crystallises from water in small, colourless needles (with $1\frac{1}{2}H_2O$), sinters at 260°, and melts slightly above 270°.

Of the foregoing substances, only three, namely, ethyl glycylglycinamidecarboxylate, diethyl glycylglycyl-leucinecarboxylate and carbonyldiglycylglycinamide, give the biuret reaction. W. A. D.

Synthesis of ζ-Aminoheptoic Acid. By ALBERT MANASSE (*Ber.*, 1902, **35**, 1367—1372).—The starting point of the synthesis of ζ-aminoheptoic acid was ε-phenoxyamylamine (see Gabriel, Abstr., 1892, 717); the latter was converted into *ε-phenoxyamylphthalimide*, $OPh\cdot[CH_2]_5\cdot N:C_8H_4O_2$, by heating with phthalic anhydride at 200°; the phthalimide crystallises in elongated leaflets melting at 72—73°. By the action of concentrated hydrobromic acid, the phenoxy-compound is converted into *ε-bromoamylphthalimide*, which forms white, flattened needles melting at 61°. *Ethyl phthaliminoamylmalonate*,

$$C_8H_4O_2:N\cdot[CH_2]_5\cdot CH(CO_2Et)_2,$$

prepared by heating the last-mentioned substance in alcoholic solution with sodium ethoxide and ethyl malonate, was ill-defined and was converted into ζ-amino-*n*-heptoic acid, $NH_2\cdot[CH_2]_6\cdot CO_2H$, by boiling with concentrated hydrobromic acid; from the hygroscopic hydrobromide thus obtained, the acid was prepared by treatment with silver oxide; it melted at 186—187° (compare Wallach, Abstr., 1900, i, 590). By heating the acid at 190° in a vacuum, a glassy, insoluble substance, $C_7H_{13}ON$ (?), was formed.

ε-*Piperidinoamylamine*, $C_5NH_{10}\cdot[CH_2]_5\cdot NH_2$, is prepared by heating ε-bromoamylphthalimide with piperidine and then boiling the product with hydrobromic acid. It is an oil boiling at 238—239° under 759 mm. pressure; the *platinichloride* crystallises in golden-yellow needles decomposing at 228°.

ε-*Anilinoamylphthalimide*, $NHPh\cdot[CH_2]_5\cdot N\colon C_8H_4O_2$, is prepared from aniline and ε-bromoamylphthalimide; it crystallises in pale yellow needles, melts at 113—114°, and dissolves in most organic solvents; by boiling with hydrochloric acid, it yields the *hydrochloride* of ε-anilinoamylamine, which forms needles melting at 218°. By the action of alcoholic potassium hydrosulphide on ε-bromoamylphthalimide, a mixture of sulphide and mercaptan is formed; the latter, ε-*phthaliminoamyl mercaptan*, $C_8H_4O_2\colon NO\cdot[CH_2]_5\cdot SH$, crystallises in white needles melting at 49·5° and is decomposed into phthalic acid and aminoamyl mercaptan by boiling hydrochloric acid. ε-*Phthaliminoamyl disulphide*, $(C_8H_4O_2\colon N\cdot[CH_2]_5\cdot)_2S_2$, prepared by the action of iodine on the mercaptan just described, melts at 60°; ε-*phthaliminoamyl sulphide*, $(C_8H_4O_2\colon N\cdot[CH_2]_5\cdot)_2S$, is prepared by the action of ε-bromoamylphthalimide on the sodium derivative of the mercaptan; it crystallises in slender needles melting at 98°. K. J. P. O.

Anhydrides of α-Amino-fatty Acids. By E. HOYER (*Zeit. physiol. Chem.*, 1902, **34**, 347—352. Compare Cohn, Abstr., 1900, i, 466).—2 : 5-Dimethylpiperazine (Bamberger and Einhorn, Abstr., 1897, i, 259) is obtained when lactimide, prepared by Fischer's method, is reduced with sodium and alcohol. This confirms Cohn's results.

J. J. S.

Synthesis of αε-Diaminohexoic Acid. By EMIL FISCHER and FRITZ WEIGERT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 270—275).—Ethyl γ-cyanopropylmalonate, when treated with ethyl nitrite in the cold, gives ethyl *α-oximino-δ-cyanovalerate*,

$$CN\cdot CH_2\cdot CH_2\cdot CH_2\cdot C(NOH)\cdot CO_2Et,$$

at first as an oil, which soon solidifies, and then melts at 74°. When reduced with sodium in alcoholic solution, this compound gives *αε-diaminohexoic acid*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, which was isolated by successive transformations into the phosphotungstate and picrate. The *picrate* can be crystallised from hot water in thick needles which darken at 230°. The *hydrochloride*, prepared from the picrate by means of hydrochloric acid, was obtained in the crystalline form, softens at 182°, and melts between 183° and 186° (corr.). The *phenylcarbimide* has also been prepared from the hydrochloride; it is formed in colourless needles melting at 182—185° (corr.).

These derivatives of αε-diaminohexoic acid have been compared with the corresponding compounds of natural lysine; the only observable differences are in the optical activity (the synthetical substances being inactive) and, slightly, in the melting points. The authors therefore regard this acid as *r*-lysine. J. McC.

Constitution of the so-called Nitrosourethane. By Julius W. Brühl (*Ber.*, 1902, **35**, 1148—1152).—The refractive index of solutions of nitrosourethane in methyl or ethyl alcohol and in ethyl acetate was determined. From these values, the molecular refraction was obtained of nitroso-urethane; in methyl alcohol, $[n]_\alpha$ 27·18 and $[n]_D$ 27·49; in ethyl alcohol, $[n]_\alpha$ 26·32 and $[n]_D$ 26·51; in ethyl acetate, $[n]_\alpha$ 26·22 and $[n]_D$ 26·04; or as mean value, $[n]_\alpha$ 26·57 and $[n]_D$ 26·68.

Owing to the colour of the solutions, the molecular dispersion could not be determined. The molecular refraction of the group N_2O is obtained by subtracting molecular refraction (calculated) of the complex, $C_3H_6O''O$, from the experimental value for nitrosourethane; it amounts to 8·87 for $[n]_\alpha$ and 8·90 for $[n]_D$; the values 9·28 and 9·35 were respectively obtained from measurements of the refractive index of nitrosoethylurethane (Abstr., 1898, ii, 362). Nitrosourethane and nitrosoethylurethane must consequently possess a similar constitution. Since the value for N_2O in the case of these substances differs widely from that found in the case of nitrosodialkylamines, it is concluded that nitrosourethane is diazourethane, $\left.\begin{matrix}N\\|\\O\end{matrix}\right>NH\cdot CO_2Et$, and nitrosoethylurethane, diazoethylurethane, $\left.\begin{matrix}N\\|\\O\end{matrix}\right>NEt\cdot CO_2Et$ (compare Hantzsch, Abstr., 1899, i, 685, and this vol., i, 222).

K. J. P. O.

Action of Alkyl Haloids on the Thiocarbonates of Secondary Amines [Tetra-alkylformocarbothialdines]. By Marcel Delépine (*Compt. rend.*, 1902, **134**, 714—716. Compare Abstr., 1901, i, 518, and this vol., i, 199).—Dialkylthiourethanes, $NR_2\cdot CS\cdot SR$, are obtained when an alkyl haloid (1 mol.) is added to an alcoholic solution of a secondary amine (1 mol.) and carbon disulphide (1 mol.); the reaction proceeds with development of heat and is complete after an hour; the mixture is poured into water, when the thiourethane separates as crystals or as an oil. The reaction is $NR_2\cdot CS\cdot S\cdot NH_2R_2 + R'X = NR_2\cdot CS\cdot SR' + NH_2R_2X$. The dialkylthiourethanes are pale yellow, crystalline solids of low melting point, which are destitute of basic properties, and thus differ from the isomeric iminothiocarbonic esters (*loc. cit.*), than which they have a higher boiling point and a higher sp. gr.; their odour resembles that of phenols:

Constitution.	Sp. gr. 0°/4°.	Melting point.	Boiling point.
$NMe_2\cdot CS_2Me$	—	47°	243°
$NMe_2\cdot CS_2Et$	1·1255	47	252
$NEt_2\cdot CS_2Me$	1·0977	2	256
$NPr_2^{\alpha}\cdot CS_2Me$	1·0475	0	275

The *piperidyl* derivative, $C_5NH_{10}\cdot CS_2Me$, melts at 33—34°; the *hydroisoquinoline* derivative, $C_9NH_{10}\cdot CS_2Me$, at 70°; the *dibenzyl* derivative, $N(CH_2Ph)_2\cdot CS_2Me$, at 55°, and the p-*nitrobenzyl* derivative,

$$NPr_2^{\alpha}\cdot CS_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

at 60°. These thiourethanes are only attacked by ammonia and amines at 300°. On oxidation with nitric acid, a secondary amine, carbon dioxide, sulphuric acid, and an alkylsulphonic acid are produced. On reduction of the compound $NMe_2 \cdot CS_2Me$ with sodium and absolute alcohol, sulphur, sodium mercaptide, trimethylamine, and dimethylmethylenediamine, $CH_2(NMe_2)_2$, are obtained. K. J. P. O.

Alkali Cyanamides. DEUTSCHE GOLD- & SILBER-SCHEIDE-ANSTALT (D.R.-P. 124977).—Sodium cyanamide, CN_2Na_2, is produced either by adding sodamide gradually to fused sodium cyanide or by passing dry ammonia into a mixture of molten cyanide and metallic sodium. Potassium cyanamide, CN_2K_2, is prepared from potassamide and potassium cyanide, whilst mixtures of sodamide and potassium cyanide or potassamide and sodium cyanide yield the sodium potassium cyanamide, CN_2NaK. G. T. M.

New Method for Characterising Pseudo-acids applied to the Alkyl Oximinocyanoacetates. By PAUL TH. MULLER (*Compt. rend.*, 1902, **134**, 475—476).—The alkyl oximinocyanoacetates containing the *iso*nitroso-radicle and the negative group cyanogen, have distinctly acid properties. Their electric conductivity is comparable with that of acetic acid; they can be titrated with alkali hydroxides in the presence of phenolphthalein, and their alkali salts do not undergo hydrolytic dissociation. Determinations of the molecular refraction of these substances and their sodium salts with respect to the α- and γ-hydrogen lines and the D-sodium line show that the values of these constants for the free acids are about 3·26 units lower than the corresponding numbers obtained with the salts. The results are tabulated. G. T. M.

The Pseudo-acids. By PAUL TH. MULLER (*Compt. rend.*, 1902, **134**, 664—665).—The equation representing the neutralisation of any acid by sodium hydroxide being $RH + NaOH = RNa + H_2O$, then, on applying to this system the law of mixtures, the following relationship between the molecular refractions of reagents and product is obtained, namely, refraction RNa − refraction RH = refraction NaOH − refraction H_2O = a constant K. The values of this constant vary between 1·50 and 1·60, and the law is found to hold in the case of a large number of acids resembling acetic acid. If, however, the structure of the radicle R varies during neutralisation, the generalisation is no longer applicable, and the values of K, experimentally determined, differ considerably from 1·55. Abnormal values of the constant were obtained with *iso*nitrosoacetone, *iso*nitrosocamphor, and the esters of oximinocyanoacetic and *iso*nitrosomalonic acids (compare preceding abstract); similar variations were observed in the molecular dispersion. These substances fall into the category of pseudo-acids, their constitution undergoing transformation during their conversion into neutral salts. G. T. M.

Aminoacetonitrile. By AUGUST KLAGES (*J. pr. Chem.*, 1902, [ii], **65**, 188—197).—*Aminoacetonitrile*, $NH_2 \cdot CH_2 \cdot CN$, obtained by treating the cyanohydrin of formic acid with cold alcoholic ammonia, is a colourless oil which boils at (about) 58° under 15 mm. pressure and forms a *hydrochloride* crystallising from alcohol and melting at 165°. With phenylcarbimide, it yields *phenylhydantonitrile*, $NHPh\cdot CO\cdot NH\cdot CH_2\cdot CN$, which crystallises in lustrous leaflets and melts at 165°. *Hippuronitrile* crystallises from alcohol and water in lustrous leaflets and melts at 144°. *Cinnamoylaminoacetonitrile*, $CHPh\colon CH\cdot CO\cdot NH\cdot CH_2\cdot CN$, crystallises in laminæ or needles, melts at 154°, and when boiled with alcoholic hydrogen chloride yields the corresponding *ester*; this melts at 108° and is easily hydrolysed to the *acid*, which crystallises in needles or laminæ melting at 193°. Formaldehyde and aminoacetonitrile condense to form methyleneaminoacetonitrile (m. p. 129°), which, from cryoscopic determinations in naphthalene and chloroform, is a bimolecular compound; the unimolecular *compound* melts at 82—83°, and the corresponding *benzylidene* derivative at 72°.

Diethylaminoacetonitrile, $NEt_2\cdot CH_2\cdot CN$, obtained when aminoacetonitrile is boiled with diethylamine for 6 hours, is a colourless liquid with a camphor-like odour; it boils at 70—71° under 24 mm. pressure and forms a *hydrochloride* which crystallises in colourless, lustrous needles melting at 192°. The *methiodide* crystallises from alcohol in colourless needles and melts at 205°. The *aurichloride* of the nitrile of methyldiethylbetaine, $C_7H_{14}N_2,HAuCl_4$, crystallises from water and melts at 99—100°. The *ethiodide* crystallises from alcohol, melts at 179°, and when treated with moist silver oxide yields a *base* which forms a crystalline *picrate*, *aurichloride*, and *mercurichloride*.

α-Diethylaminopropiononitrile, $NEt_2\cdot CHMe\cdot CN$, obtained from lactonitrile and diethylamine, is an oil which boils at 81° under 27 mm. pressure and has a sp. gr. 0·857 at 16°/4°. The *aurichloride* crystallises in needles melting at 126°, and the *picrate* melts at 102°. The *methiodide* melts and decomposes at 212°, and the methochloride forms an *aurichloride* which melts at 109—110°. R. H. P.

Preparation of Hydrogen Cyanide in the Electric Furnace and Transformation of Atmospheric Nitrogen into Ammonia. By HANS HOYERMANN (*Chem. Zeit.*, 1902, **26**, 70—71).—In view of the observations made by Berthelot and by Moissan that hydrogen cyanide can be obtained from acetylene and nitrogen, the author led mixtures of these gases through hollow carbon electrodes into the arc light, and found that hydrogen cyanide is formed in large quantity. It is also produced from acetylene and ammonia, or from benzene and nitrogen. The best result is obtained when the mixture contains 2 volumes of nitrogen per volume of acetylene.

When a mixture of calcium fluoride and aluminium is heated to redness in a carbon crucible, a residue is obtained which, when treated with hot water, gives off a large quantity of ammonia. Aluminium fluoride is volatilised, and the residual mass apparently consists of calcium nitride (Ca_3N_2), the nitrogen being obtained from the air. The same mixture, heated in a porcelain tube in a current of nitrogen, did not give the same result. J. McC.

Basic Properties of Oxygen. III. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, **35**, 1201—1212. Compare this vol., i, 112).—I. *Quadrivalency of oxygen.*—It seems probable that the compound of ether with magnesium methiodide, $MgMe\cdot OEt_2I$, described by Grignard, is a true oxonium compound of simple type, the existence of such a compound, whilst no compound of the type R_3OI is known, being rendered possible by the fact that the group MgMe has a greater affinity for oxygen and is more easily separated from iodine than the methyl group itself.

II. *Salts of Ferrocyanic Acid with the simplest Organic Oxygen Compounds.*—When an alcoholic solution of ferrocyanic acid is evaporated slowly, an oil is left which solidifies in large, transparent tablets containing 3 mols. of alcohol, and decomposes in the air. The oil itself probably contains 4 mols. of alcohol. This renders it probable that the crystalline compound obtained by Buff (*Annalen*, 1854, **91**, 253) by passing hydrogen chloride into an alcoholic solution of ferrocyanic acid is in reality a *double* salt of the alcohol compound of ferrocyanic acid with alcohol hydrochloride, $Fe(CN)_6H_4(EtOH)_4 + 2Et{\cdot}OH,HCl$, and the properties of the compound agree fully with this constitution. Ferrocyanic acid also forms a *compound* with methyl alcohol which crystallises in lustrous, efflorescent needles.

Similarly, the compound described by Than (*Annalen*, 1858, **107**, 315) as ethyl platinocyanide with water of crystallisation, is in reality the salt of cyanoplatinous acid with ethyl alcohol, $Pt(CN)_4H_2,2EtOH$, and since this acid forms very stable oxonium salts it will probably be of great value as a reagent.

Ferrocyanic acid not only combines with alcohol and with ether, as previously shown, but also forms mixed compounds. When a solution of the acid in methyl alcohol is precipitated by ether, the *compound*, $H_4Fe(CN)_6,C_4H_{10}O,CH_4O$, separates out in rhombic plates. It is probable that the substance obtained by Buff by dissolving his compound in alcohol and precipitating with ether was also a substance of this class.

When acetone is added to a solution of ferrocyanic acid in methyl alcohol, a *compound* of ferrocyanic acid with acetone, $H_4Fe(CN)_6,C_3H_6O$, is formed, which crystallises in plates. The complex acids may conveniently be prepared from the acidified solutions of their salts by treatment with cineol, followed by purification of the resulting oxonium salt, and removal of the cineol by distillation or extraction with ether.

III. *Compounds of Phenols with Organic Oxygen Compounds.*—Many compounds of phenols with bases are already known. Pyridine unites with 1 mol. of quinol to form the *compound* $C_5H_5N,C_6H_6O_2$, which crystallises in needles and melts at 81—83°. Quinoline unites with quinol to form the *compound* $2C_9H_7N,C_6H_6O_2$, which crystallises in flat prisms melting at 98—99°. With pyrogallol, it forms the *compound* $3C_9H_7N,C_6H_6O_3$, crystallising in flat prisms and melting at 56—57°.

Similar compounds are also formed by phenols with oxygen compounds. Cineol and resorcinol form the *compound* $C_6H_6O_2,2C_{10}H_{18}O$, which crystallises in long, lustrous, rhombic plates melting at 80—85°. Cineol and pyrogallol form the *compound* $C_6H_6O_3,C_{10}H_{18}O$, which crystallises in prisms and has no definite melting point. The *compound* of quinol with ethyl oxalate, $C_6H_6O_2,C_6H_{10}O_4$, forms large plates and has no definite melting point. The *compound* of quinol and cinnamaldehyde, $C_6H_6O_2,2C_9H_8O$, forms faintly yellow needles melting at

53—55°. Quinol and dimethylpyrone form the *compound*

$$C_6H_6O_2,C_7H_8O_2,$$

which crystallises in prisms and melts at 107—109°. The *compound* of quinol with *tert.*amyl alcohol, $C_6H_6O_2,C_5H_{12}O$, is unstable and loses the alcohol when heated. The *compound* of quinol with trimethylcarbinol, $C_6H_6O_2,C_4H_{10}O$, resembles that with *tert.*amyl alcohol.

IV. *Compounds of Oxalic Acid with Oxygen Compounds.—Cinnamaldehyde oxalate*, $C_2H_2O_4,2C_9H_8O$, forms tetrahedral crystals melting at 60—62°. *Cineol oxalate*, $C_2H_2O_4,2C_{10}H_{18}O$, decomposes at 50°.

A. H.

Preparation of a Soluble Prussian Blue. By J. Matuschek (*Chem. Zeit.*, 1902, **26**, 92—93).—On heating a solution of potassium ferricyanide with oxalic acid, a blue colour is developed, and on evaporation a blue deposit is obtained. The blue substance, which has the formula $Fe_7(CN)_{18}$, is formed according to the equation: $14K_3Fe(CN)_6 + 42C_2H_2O_4 + 3H_2O = 2Fe_7(CN)_{18} + 42C_2O_4HK + 48HCN + 3O$. Some decomposition also takes place in another way, for the solution contains, besides this blue compound, a ferric salt which imparts a yellow colour to it. The blue compound is easily soluble in water, but is insoluble in alcohol. It retains the potassium hydrogen oxalate simultaneously deposited with great tenacity, so that this can only be removed by repeated washing with dilute alcohol.

A similar decomposition can be brought about by sunlight instead of heat, and it has been proved that the oxygen of the air takes no part in the reaction.

J. McC.

New Reactions of Organometallic Compounds. V. By Edmond E. Blaise (*Compt. rend.*, 1902, **134**, 551—553. Compare this vol., i, 164).—Magnesium alkyl bromides react with ethylene oxide, forming together with a small amount of a primary alcohol of the type $R{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (compare Grignard and Tissier, this vol., i, 198), mainly the bromohydrin of glycol; the addition of the magnesium alkyl bromide to the ethylene oxide takes place in two ways: (i) $R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}MgBr$ and (ii) $R{\cdot}Mg{\cdot}O{\cdot}CH_2{\cdot}CH_2Br$.

The esters of α-brominated fatty acids condense with trioxymethylene in the presence of zinc, producing the esters of β-hydroxy-acids; thus from ethyl α-bromo*iso*butyrate is obtained *ethyl hydroxypivalate*, $OH{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2Et$, which boils at 85—87° under 16 mm. pressure, and yields an *acid* crystallising in long needles. With phosphorus pentabromide, *ethyl bromopivalate* is obtained as an oil of agreeable odour boiling at 89—90° under 25 mm. pressure.

K. J. P. O.

Chemistry of Mercury. III. By Heinrich Ley and Konrad Schaefer (*Ber.*, 1902, **35**, 1309—1316. Compare Abstr., 1899, ii, 485; 1900, i, 382).—The mercuric derivatives of the organic oxy-acids undergo hydrolytic dissociation in aqueous solutions, and their electrical conductivities are of the same order as those of the acids themselves.

The stability of the mercury-nitrogen linking is far greater than that of the metal with oxygen, and the aqueous solutions of the mercuric derivatives of amides, imides, and similarly constituted substances do not give the reactions of the Hg″ ion. The equilibrium of the system $2R\cdot CO\cdot NH_2 + HgCl_2 \rightleftarrows 2HCl + (R\cdot CO\cdot NH)_2Hg$ was studied in the case of the homologous amides of the acetic acid series by the electrolytic method; for since the ionisation of mercuric chloride is very slight, the agent chiefly concerned in the transmission of the current is the hydrochloric acid, and hence the electrical conductivity is a measure of the amount of mercury derivative produced. The electrical conductivities μ_{64} of solutions containing $N/32$ $HgCl_2$ and $N/16$ amide were 7·8, 5·2, 5·1, and 5·3 for formamide and its successive homologues up to butyramide. The *mercury* derivative, $Hg(NH\cdot CO\cdot C_3H_7)_2$, of the latter amide separates from water as a white, crystalline mass. A more dilute solution was necessary in the case of chloroacetamide, and the system $N/64$ $HgCl_2 + N/32$ $CH_2Cl\cdot CO\cdot NH_2$ gave $8·8\mu_{128}$. The substitution of cyanogen for chlorine increases the tendency to the formation of a mercury derivative, the system $N/32$ $HgCl_2 +$ $N/16$ $CN\cdot CH_2\cdot CO\cdot NH_2$ giving $53·5\mu_{64}$. This abnormal result accords with the behaviour of the amide towards freshly precipitated mercuric oxide, the amount of the latter substance dissolved being in excess of that required by the formula $Hg(NH\cdot CO\cdot CH_2\cdot CN)_2$, and corresponding more nearly with $CN\cdot CH(Hg\cdot OH)\cdot CO\cdot NH_2$. The values of μ_{64} obtained with urea, urethane, and biuret are 5·3, 5·2, and 5·8 respectively. The system $N/32$ $HgCl_2 + N/16$ succinimide gives $40·2\mu_{64}$, whilst the value of the constant with camphorimide is 45·3. These results indicate that the stability of the mercury compounds of imides exceeds that of the corresponding derivatives of the amides.

The electrical conductivity of the system $N/32$ $HgCN_2 + N/16$ HCl is 355, whilst that of the acid is 369; the amount of hydrogen cyanide set free, although appreciable, is very small. When, however, nitric acid is employed, there is no appreciable metathesis, the electrical conductivity, $355·1\mu_{32}$, being identical with that of the acid itself. These results place mercuric cyanide entirely outside the category of imides and points to the existence in this compound of a stable linking between mercury and carbon. G. T. M.

Silver Derivatives of Acid Amides and Imides. By HEINRICH LEY and KONRAD SCHAEFER (*Ber.*, 1902, **35**, 1316—1319. Compare Titherley, Trans., 1901, **79**, 391).—The yellow precipitate which is produced on adding silver nitrate to an aqueous or dilute alcoholic solution of urethane in the presence of sodium hydroxide, rapidly becomes orange coloured, and finally, when dried, forms a brick-red powder. The red salt probably contains silver attached to nitrogen; it dissolves in excess of sodium hydroxide solution, yielding a solution from which the original substance is reprecipitated on dilution.

Phenylurethane and the corresponding benzyl analogue, when treated with silver nitrate and a small quantity of sodium hydroxide, yield deep red precipitates which rapidly become black. G. T. M.

Compounds of Antimony Pentachloride with Organic Acids. By ARTHUR ROSENHEIM and WILLY LOEWENSTAMM (*Ber.*, 1902, **35**, 1115—1130. Compare this vol., i, 68).—With antimony pentachloride, organic acids and hydroxy-acids form crystalline additive compounds which contain 1 mol. of the pentachloride for each carboxyl group. On heating, these compounds decompose, yielding acid chlorides. The additive compounds derived from hydroxy-acids (and dibasic acids) give substances in which the hydroxylic hydrogen has been replaced by the group $\cdot SbCl_4$. Esters yield similar additive compounds. The number of mols. of antimony pentachloride in the additive compound appears to depend on the number of carbonyl groups present; thus, ethyl acetoacetate combines with $2SbCl_5$, whereas ethyl metacarbonate combines only with $SbCl_5$. The view is expressed that in the additive compounds the oxygen of the carbonyl group has become quadrivalent.

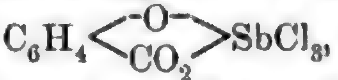
The additive compounds are prepared by mixing chloroform solutions of mol. proportions of the acid (or ester) and antimony pentachloride, and are very hygroscopic, crystalline substances, readily soluble in chloroform, carbon tetrachloride, &c. The compounds with *acetic acid*, $CH_3\cdot CO_2H,SbCl_5$, and with *ethyl acetate*, $CH_3\cdot CO_2Et,SbCl_5$, crystallise in white needles; those with *propionic* and *valeric* acids cannot be isolated, and when kept in chloroform solution are converted into *additive* compounds of antimony pentachloride and the acid chlorides, $CH_2Me\cdot COCl,SbCl_5$ and $CH_3\cdot[CH_2]_3\cdot COCl,SbCl_5$, which crystallise in hygroscopic, transparent plates.

The *compound* with benzoic acid, $C_6H_5\cdot CO_2H,SbCl_5$, forms stable, white needles, melting at 71°, and on heating yields benzoyl chloride. Phenylacetic acid gives an unstable *product* crystallising in yellow needles.

The additive compound with oxalic acid (*loc. cit.*) yields a substance to which is now ascribed the formula $(CO_2\cdot SbCl_4)_2$, and not that previously stated (compare Anschütz and Evans, Abstr., 1888, i, 424). By addition of a chloroform solution of antimony pentachloride to methyl oxalate suspended in boiling chloroform, a *compound*, $C_2O_4(CH_2\cdot SbCl_4)_2$, is obtained which crystallises in white, hygroscopic plates. Ethyl oxalate yields a crystalline *additive* compound, $C_2O_4Et_2,2SbCl_5$, which easily loses hydrogen chloride with the production of a *substance*, $C_2O_4(CH_2\cdot CH_2\cdot SbCl_4)_2$, crystallising in white plates.

From malonic acid, a *compound*, $CH_2(CO_2H)_2,SbCl_5$, crystallising in pale brown needles was prepared with some difficulty; ethyl malonate yielded with ease a *compound*, $CH_2(CO_2Et)_2,2SbCl_5$, which formed very hygroscopic, white needles. From succinic acid was obtained a stable *additive* product with $2SbCl_5$, crystallising in needles, and from ethyl succinate a *compound*, $C_2H_4(CO_2Et)_2,2SbCl_5$, also crystallising in needles. Phthalic acid yields the *compound* $C_6H_4(CO_2\cdot SbCl_4)_2$, which forms white, prismatic crystals.

Ethyl carbonate gives a *compound* with $SbCl_5$ crystallising in hygroscopic needles. The following hydroxy-acids react with antimony pentachloride with evolution of hydrogen chloride: lactic acid yields a *compound*, $SbCl_4\cdot O\cdot CHMe\cdot CO_2H$, forming prisms which decompose at 132°; ethyl lactate, the corresponding *ethyl* ester crystallising in prismatic plates; mandelic acid, a *compound*, $SbCl_4\cdot O\cdot CHPh\cdot CO_2H$, crystallising in needles. From salicylic acid, an additive *compound*,

$OH\cdot C_6H_4\cdot CO_2H,SbCl_5$, is obtained, crystallising in pale yellow needles which very easily decompose into hydrogen chloride, and the acid, $SbCl_4\cdot O\cdot C_6H_4\cdot CO_2H$, which crystallises in very soluble, reddish-yellow needles, melts at 154°, decomposes at about 185°, does not give a reaction with ferric chloride, and forms a series of salts; the *lead* and *thallium* salts form dark yellow, insoluble crystals, the *silver* salt an amorphous yellow powder; the salts of the alkaline earths are soluble and crystalline; the *potassium* salt forms small, lustrous, red prisms, the *ammonium* salt reddish-purple prisms, the *cæsium* salt insoluble, yellow needles. When mol. proportions of antimony pentachloride and salicylic acid are heated together for many hours in chloroform solution, a *compound*,  $C_6H_4<\overset{-O-}{\underset{CO_2}{}}>SbCl_3$, is obtained; it crystallises in slender, orange-yellow, insoluble needles melting and decomposing at 194°, and is only decomposed after prolonged boiling with alkalis. Methyl salicylate and antimony pentachloride form an *additive* compound, $OH\cdot C_6H_4\cdot CO_2Me,SbCl_5$, crystallising in dark yellow needles; this is readily converted into the *ester*, $SbCl_4\cdot O\cdot C_6H_4\cdot CO_2Me$, which forms prisms resembling potassium dichromate and melting at 135°; the *ethyl* ester melts at 121°.

Tartaric acid yields an *acid*, $C_2H_2(O\cdot SbCl_4)_2(CO_2H)_2$, crystallising in white, very hygroscopic needles; the *ethyl* ester forms aggregates of hygroscopic prisms.

Ethyl citrate yields an *additive* compound,

$$CO_2Et\cdot C(OH)(CH_2\cdot CO_2Et)_2,3SbCl_5,$$

crystallising in large, white needles.

Ethyl acetoacetate gives an *additive* compound with $2SbCl_5$ crystallising in white, hygroscopic needles.

Tungsten hexachloride does not form additive compounds, but reacts with hydroxy-acids with evolution of hydrogen chloride, thus with methyl salicylate a *compound*, $WCl_4(O\cdot C_6H_4\cdot CO_2Me)_2$, is formed; it crystallises in large, deep red crystals. Tungsten pentachloride, on the other hand, readily forms additive compounds with development of heat.

K. J. P. O.

Di*cyclo*hexyl and Dimethyldi*cyclo*hexyl. By NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 221—226).—*Dicyclohexyl*, $C_6H_{11}\cdot C_6H_{11}$, prepared by the action of sodium on iodo*cyclo*hexane, is an oily, faintly-smelling liquid, which boils at 235° under 752 mm. pressure and solidifies to a crystalline mass in a mixture of ice and salt; it has the sp. gr. is 0·8777 at 0°/0° and 0·8644 at 20°/0°. It is not acted on by alkaline permanganate or by a mixture of sulphuric and nitric acids.

Dimethyldicyclohexyl, $C_6H_{10}Me\cdot C_6H_{10}Me$, obtained by the action of sodium on iodomethyl*cyclo*hexane, boils undecomposed at 264° under 761 mm. pressure and at 148—149° under 30 mm. pressure, and solidifies to a glassy mass when cooled in liquid air; it has the sp. gr. 0·8924 at 0°/0° and 0·8789 at 20°/0°, and $[\alpha]_D$ −3°44′. In its behaviour towards reagents, it resembles di*cyclo*hexyl.

The methods of preparation of these compounds give rise also to considerable quantities of the corresponding naphthenes and naphthylenes; the latter are formed by the splitting off of hydrogen iodide from the iodonaphthene, whilst the reducing action of sodium in presence of hydriodic acid yields the naphthenes. T. H. P.

$\Delta^{1:3}$-Dihydrotoluene and a Modification of Wagner's Oxidation Rule. By Carl D. Harries [and, in part, Ernst Atkinson] (*Ber.*, 1902, **35**, 1166—1176).—Methyl*cyclo*hexenonehydroxylamino-oxime (Abstr., 1901, i, 194), when oxidised by mercuric oxide, yields a *mononitroso*-compound, $C_7H_{12}O_2N_2$, which is a white, crystalline substance melting to a blue oil at 106—108°; the *dibenzoyl* derivative of the oxime is a colourless oil, and the *oxalate* a white, crystalline mass. Hexahydro-*m*-tolylenediamine (*loc. cit.*) forms a crystalline *nitrate* and a *dibenzoyl* derivative which melts between 247° and 270°. *Hexahydro-*m*-tolylenediaminediphenylcarbamide*, $C_{21}H_{26}O_2N_4$, crystallises in rhombic rods and melts between 210° and 240°. $\Delta^{1:3}$-Dihydrotoluene (*loc. cit.*), when oxidised with permanganate in aqueous solution, yields oxalic and succinic acids, and, when in aqueous acetone solution, dihydroxymethyl*cyclo*hexanone (see this vol., i, 378).

A dihydro-*m*-xylene has been prepared from the hydroxylamino-oxime of dimethyl*cyclo*hexenone by methods analogous to those previously described (*loc. cit.*). *Hexahydro-*m*-xylylenediamine* is a colourless liquid which boils at 103—105° under 27 mm. pressure, absorbs carbon dioxide, and forms a *hydrochloride* which crystallises in colourless, rhombic, pyramidal prisms with a high melting point.

*Hexahydro-*m*-xylylenediaminediphenylcarbamide* crystallises in needles and melts at 247°. The *phosphate* of the diamine is a syrup, and when distilled, yields the *dihydro-xylene*, which is a light yellow oil boiling at 126—128° under a pressure of 750 mm.

From a discussion of the results, it is shown that the products of the oxidation of an unsaturated compound do not necessarily contain as many "oxidised" carbon atoms as those which were doubly linked in the original compound. It also follows from this that terpinene is $\Delta^{1:4}$-menthanediene, and is identical with the synthetical terpene prepared by Baeyer from ethyl succinylosuccinate. R. H. P.

The Configuration of the Benzene Nucleus. By Wilhelm Vaubel (*Chem. Zeit.*, 1902, **26**, 244—245).—Objection is taken to the conclusions arrived at by Graebe (this vol., i, 209) as to the figure representing the benzene molecule. Facts are stated in support of the Vaubel-Marsh configuration, three tetrahedra above and three below a plane, which explains (*a*) the different behaviour of *o*- and *p*-derivatives from that of the *m*-compounds; (*b*) the influence of *m*-substitution; and (*c*) that molecular rearrangement may take place and thus evidence of enantiomorphism is in most cases lost. The author regards his figure as satisfactorily accounting for the oscillating single and double bond of Kekulé's hypothesis. J. McC.

Action of Copper Nitrate on Benzene. By Nicolai P. Wassilieff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 33—37. Compare *J. Russ. Phys. Chem. Soc.*, 1894, **26**).—The reaction between copper nitrate and benzene proceeds slowly at 100°, but the best results are obtained by heating in sealed tubes at 170—190° for 12—18 hours.

The products obtained are nitrobenzene, picric acid, several nitro- and other compounds not yet investigated, and an *acid* of the $C_nH_{2n-2}O_{2n}$ series. This acid melts in a sealed capillary tube at 98—100° and dissolves readily in water or alcohol and slightly in ether; when heated with alcohol and hydrochloric acid, it yields ethyl oxalate. T. H. P.

Reaction between Benzene and Cellulose. By A. M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 231—235).—When a concentrated sulphuric acid solution of Swedish filter paper is shaken in a separating funnel with benzene, the latter reacts with the cellulose, and on decomposing the solution with water a dark brown powder is obtained which is insoluble in the ordinary solvents, but is partially soluble in cold nitric acid, the portion not dissolved undergoing nitration. From the analysis of different fractions of the nitrated compound, the author supposes that the first product of the reaction between the benzene and cellulose is tetraphenylcellulose, $C_6H_6O_5Ph_4$, and that this undergoes sulphonation and, on treatment with nitric acid, nitration. The two following nitrated products were separated and analysed: (1) $C_{360}H_{292}O_{103}N_{20}S$, resulting from the introduction into 12 tetraphenylcellulose molecules of 20 nitro-groups and one SO_3H group in place of 21 hydrogen atoms; when dried at 105—110°, this compound loses $12H_2O$ and assumes the formula $C_{360}H_{268}O_{91}N_{20}S$; (2) $C_{360}H_{288}O_{114}N_{24}S_2$, obtained from 12 molecules of tetraphenylcellulose by the replacement of 24 hydrogen atoms by NO_2 groups and of two hydrogen atoms by SO_3H groups. T. H. P.

Derivatives of 3:4:5-Tribromonitrobenzene. By C. LORING JACKSON and A. H. FISKE (*Ber.*, 1902, **35**, 1130—1133).—By the action of sodium methoxide in the cold, 3:4:5-tribromonitrobenzene is converted into 1-methoxy-2:6-dibromo-4-nitrobenzene (m. p. 122°), which, on reduction, yields a *base*, $OMe\cdot C_6H_2Br_2\cdot NH_2$, melting at 64—65° (compare Staedel, Abstr., 1883, 663); the *hydrochloride* was analysed. When boiled with sodium methoxide in methyl alcoholic solution, the tribromonitrobenzene is transformed into a 3:5-*dibromo*-4-*methoxyazoxybenzene*, $ON_2(C_6H_2Br_2\cdot OMe)_2$, which crystallises in pale yellow needles melting at 214°.

Sodium ethoxide in the cold converts the tribromonitrobenzene into 1-ethoxy-2:6-dibromo-4-nitrobenzene (m. p. 58—59°), which, on reduction, yields the corresponding amino-derivative (m. p. 107°); Staedel (*loc. cit.*) gives 108° and 67° as the melting points respectively of these two substances. When boiled with sodium ethoxide in ethyl alcoholic solution, a 3:5-*dibromo*-4-*ethoxyazoxybenzene* is obtained, crystallising in pale yellow needles melting at 163°.

On treatment with a boiling mixture of fuming nitric and sulphuric acids, 3:4:5-*tribromo*-1:2-*dinitrobenzene*, $C_6HBr_3(NO_2)_2$, is formed from tribromonitrobenzene; it crystallises in large, monoclinic prisms melting at 160°. K. J. P. O.

Monoiodo- and Monobromo-derivatives of the Aromatic Hydrocarbons. KALLE and Co. (D.R.-P. 123746).—Sulphur iodide, S_2I_2, and the corresponding bromide react with aromatic hydrocarbons in the presence of nitric acid, giving rise to iodo- and bromo-derivatives respectively. The mono-substituted compounds are exclusively produced except in the case of durene which furnishes a dibromo-derivative.

Benzene, *o*-xylene, mesitylene, and naphthalene, when dissolved in light petroleum and warmed with nitric acid of sp. gr. 1·34 and powdered sulphur iodide, yield the corresponding monoiodo-derivatives, naphthalene giving rise to α-iodonaphthalene together with smaller quantities of the β-iodo-compound and α-nitronaphthalene.

G. T. M.

Toluene-*o*-sulphonic Chloride and the *o*-Sulphonic Chlorides of Ethereal Benzoates. BASLER CHEMISCHE FABRIK (D.R.-P. 124407).—Toluene-*o*-sulphonic chloride is obtained from toluene-*o*-sulphinic acid by treating this with chlorine in the presence of dilute sodium hydroxide or hydrochloric acid solution, the temperature being kept below 35°.

The *o-sulphonic chloride*, $CO_2Me·C_6H_4·SO_2Cl$, of methyl benzoate, produced in a similar manner from the *o*-sulphinic acid,

$$CO_2Me·C_6H_4SO_2H$$

(m. p. 98—99°), melts at 64—65°. G. T. M.

Preparation of Triphenylmethane. By JAMES F. NORRIS and GRACE MACLEOD (*Amer. Chem. J.*, 1901, **26**, 499—505).—Norris and Saunders (Abstr., 1901, i, 198) have shown that if the product of reaction of benzene on carbon tetrachloride in presence of aluminium chloride be purified by crystallisation, triphenylchloromethane is obtained, whilst by distillation triphenylmethane is produced. By the action of benzene on chloroform in presence of aluminium chloride, triphenylmethane is also obtained when the crude product is distilled. If the aluminium additive compound be carefully decomposed with water in presence of a large volume of carbon disulphide, then on evaporation of the carbon disulphide solution, crystals of triphenylcarbinol are obtained along with an uncrystallisable oil. When triphenylmethane is treated with aluminium chloride in carbon disulphide solution and a current of oxygen is aspirated through the mixture, crystals of triphenylcarbinol are produced as well as a thick oil. By the action of aluminium chloride on triphenylcarbinol, triphenylchloromethane is obtained. The composition of the oil produced by the reaction between benzene and chloroform is very complex and the various constituents have not yet been identified; it probably contains diphenylchloromethane.

Triphenylmethane is probably produced during the distillation as a result of the reduction of the triphenylcarbinol by the uncrystallisable oil. J. McC.

Condensation Products from 1 : 8-Dinitronaphthalene soluble in Alkali Hydroxides. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 125133).—1 : 8-Dinitronaphthalene, when heated with sodium hydroxide solutions of salicylic acid, *p*-aminosalicylic acid, and *p*-aminophenol, gives rise to condensation products which are soluble in this medium and precipitated on the addition of hydrochloric acid. G. T. M.

2 : 4-Dinitrostilbene and its Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 124681).—Although the methyl group of the nitrotoluenes and similar mononitro-derivatives does not react with aromatic aldehydes, yet condensation occurs when the nucleus contains two nitro-groups.

2 : 4-Dinitrostilbene, $C_6H_5 \cdot CH \vdots CH \cdot C_6H_3(NO_2)_2$, is produced by heating benzaldehyde and 2 : 4-dinitrotoluene at 130—140° in the presence of dry ammonia or an amine, piperidine, for example ; it separates from glacial acetic acid in yellow crystals and melts at 139—140°.

2 : 4 : 4′-*Trinitrostilbene*, $NO_2 \cdot C_6H_4 \cdot CH \vdots CH \cdot C_6H_3(NO_2)_2$, results from the condensation of 2 : 4-dinitrotoluene with *p*-nitrobenzaldehyde ; it crystallises from nitrobenzene in felted, lemon-yellow needles and melts at 240°.

2 : 4 : 3′-*Trinitrostilbene*, obtained from *m*-nitrobenzaldehyde, crystallises from glacial acetic acid in yellow needles and melts at 183—184°.

G. T. M.

Fluorene. AKTIEN GESELLSCHAFT FÜR THEER- & ERDÖL-INDUSTRIE (D.R.-P. 124150).—Fluorene reacts with potassium hydroxide at 280°, yielding a solid *potassium* derivative, $C_{13}H_9K$, which is decomposed into its generators by water. This reaction can be employed to separate the hydrocarbon from mixtures containing it. G. T. M.

Dimethylaniline Oxide. By EUGEN BAMBERGER and LEO RUDOLF (*Ber.*, 1902, **35**, 1082—1083).—This substance can be most conveniently prepared by oxidising dimethylaniline with an ice-cold diluted solution of Caro's acid, and "salting out" with sodium sulphate ; it is freed from small quantities of the latter by dissolving in alcohol and evaporating in an exhausted receiver over sulphuric acid. It fails to interact additively with hydrogen cyanide to yield dimethylaminobenzonitrile, simply effecting polymerisation of the acid to aminomalononitrile. W. A. D.

Arylsulphonimides. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 125390).—The anhydrous metallic derivative of an arylsulphonamide, when treated at 180° with an arylsulphonic chloride, yields the corresponding sulphonimide.

*Di-*p*-toluenesulphonimide*, $(C_6H_4Me \cdot SO_2)_2NH$, obtained from the sodium derivative of *p*-toluenesulphonamide and *p*-toluenesulphonic chloride, is a crystallisable substance, readily soluble in ether or alcohol, but dissolving only sparingly in water.

Di-o-toluenesulphonimide and *dibenzenesulphonimide*, produced in a similar manner, separate in needles and in crystalline aggregates respectively.

Mixed sulphonimides containing dissimilar aryl radicles are also readily prepared by the preceding method. G. T. M.

Benzylethylaniline. By GUSTAV SCHULTZ and EBERHARD BOSCH (*Ber.*, 1902, **35**, 1292—1296).—The base boils with partial decomposition at 275—298° under atmospheric pressure, and at 185·5—186·5° under 22 mm. pressure, does not solidify, and has sp. gr. 1·034 at 18·5°. The *picrate* crystallises in short prisms and melts at 114°.

m-*Nitrobenzylethylaniline*, $C_{15}H_{16}O_2N_2$, crystallises from alcohol in orange-yellow prisms and melts at 69°; a small quantity of a nitro-derivative melting at 67° is also produced. The *hydrochloride* crystallises from chloroform and melts at 186°. The *picrate* crystallises in prisms and melts at 131°. On oxidation, the base yields *m*-nitrobenzoic acid.

m-*Aminobenzylethylaniline*, $C_{15}H_{18}N_2$, is an oil which boils at 261—262° under 57—58 mm. pressure. The hydrochloride crystallises from a mixture of alcohol and ether and melts at 188—190°.

p-*Nitrosobenzylethylaniline*, $C_{15}H_{16}ON_2$, separates from ether in steel-blue crystals and melts at 62°.

p-*Aminobenzylethylaniline*, $C_{15}H_{18}N_2$, boils at 225° under 21 mm. pressure. The *hydrochloride* separates from ether as a white, hygroscopic precipitate. The *oxalate* crystallises from alcohol and melts at 168—169°. The *benzoyl* derivative crystallises in needles and melts at 124°. T. M. L.

Action of Cyanogen Bromide on Tertiary Amines. IV. By JULIUS VON BRAUN and RUDOLF SCHWARZ (*Ber.*, 1902, **35**, 1279—1288. Compare Abstr., 1900, i, 430, 641, 687).—*Benzyldipropylamine*, $C_6H_5\cdot CH_2\cdot NPr^{\alpha}_2$, prepared by heating benzyl chloride and dipropylamine at 120°, is a colourless, odourless oil and boils at 235—243°. The *hydrochloride* melts at 156°. The *platinichloride* is a reddish-yellow salt and melts at 156°. The *picrate* melts at 121°. By the action of cyanogen bromide, the base is converted into dipropylcyanamide and benzyl bromide.

Benzylisopropylaniline, $C_6H_5\cdot CH_2\cdot NPhPr^{\beta}$, from benzyl chloride and *iso*propylaniline, boils at 177—178° under 12 mm. pressure. The hydrochloride melts at 184°. The *platinichloride* separates from alcohol in reddish-yellow crystals and melts at 186°. The *picrate* crystallises from a mixture of alcohol and ether and melts at 138—140°. The base does not react with cyanogen bromide at atmospheric temperatures; at 100°, benzyl bromide, benzyl*iso*propylaniline hydrobromide, and resin are formed. Benzyldiethylamine behaves similarly, benzyl bromide being formed and the diethylcyanamide being decomposed into diethylamine. Benzylmethylaniline gave benzyl bromide and phenylmethylcyanamide.

Benzylallylaniline interacts with cyanogen bromide to form allyl bromide and *phenylbenzylcyanamide*, $C_6H_5\cdot CH_2\cdot NPh\cdot CN$, which boils at 185—195° under 12 mm. pressure, crystallises from a mixture of alcohol and ether, and melts at 60°; with ammonia and hydrogen sulphide, it gives phenylbenzylthiocarbamide.

Dibenzylallylamine, $C_3H_5\cdot N(CH_2Ph)_2$, from allyl iodide and dibenzylamine, is a colourless, odourless oil and boils at 168—170° under 10 mm. pressure; the *hydriodide* crystallises from a mixture of alcohol and ether, melts at 210°, and is not readily soluble in cold water; the *hydrochloride* melts at 259°; the *platinichloride* melts at 168—169°; the *picrate* was only obtained as an oil. With cyanogen bromide, the base gave dibenzylallylamine *hydrobromide*, which softens at 210° and melts at 227°, and dibenzylcyanamide.

It appears, therefore, that the benzyl radicle is split off more readily than methyl, ethyl, or phenyl, but less readily than the allyl radicle. T. M. L.

Phenolic Sulphurous Esters. Badische Anilin- & Soda-Fabrik (D.R.-P. 115335. Compare Abstr., 1901, i, 695, and this vol., i, 91).—Resorcinol, 1 : 8-dihydroxynaphthalene, *a*-naphtholsulphonic acids (except the 2- and 3-sulphonic acids or the disulphonic acids derived from them), *β*-naphtholsulphonic acids (except the 4-sulphonic acid and its derivatives), and 8-amino-*a*-naphthol-6-sulphonic acid, when heated with a strong solution of sodium hydrogen sulphite (40° Bé) are converted into readily soluble sulphurous esters.

The esters may also be obtained by the action of sodium hydrogen sulphite from the corresponding amino-compounds; they are hydrolysed by alkalis, yielding the phenols, and when treated with ammonia give rise to amines. Hence they may be employed either in converting amino-compounds into phenols, or in bringing about the opposite change by the replacement of hydroxyl by amidogen. G. T. M.

Phenolic Sulphurous Esters. Badische Anilin- & Soda-Fabrik (D.R.-P. 126136. Compare Abstr., 1901, i, 695, and preceding abstract).—Sodium *β*-naphthylamine-6-sulphonate and 5-hydroxy-*β*-naphthylamine-7-sulphonic acid, when heated with a large excess of sodium hydrogen sulphite solution, yield the sulphurous esters of *β*-naphthol-6-sulphonic acid and 2:5-dihydroxynaphthalene-7-sulphonic acid respectively. *m*-Phenylenediamine, when treated with the sulphite solution, gives rise to a sulphurous ester of *m*-aminophenol. G. T. M.

[4-Nitro-*p*-hydroxyphenyl-*a*-naphthylamine.] Chemische Fabrik vorm. Sandoz (D.R.-P. 123922).—1-Chloro-4-nitronaphthalene derivatives readily condense with the amino-*p*-phenol or its sulphonic acid, forming 4-nitrophenyl-*a*-naphthylamine derivatives. These nitro-amino-compounds, when heated with alkali polysulphides, yield colouring matters containing sulphur.

4 : 8-*Dinitro*-p-*hydroxyphenyl*-a-*naphthylamine*, prepared by heating together 4 : 8-dinitro-1-chloronaphthalene, *p*-aminophenol, and sodium acetate in alcoholic solution at 120—140°, is precipitated by acids from the product as a reddish-brown powder; it crystallises from most organic solvents in needles insoluble in water. The sulphonated derivatives of this compound are obtained in a similar manner. G. T. M.

Sulphonic Acids of *as*-Naphthalenoid Thiocarbamides containing Free Hydroxyl Groups. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 123886).—*as*-Thiocarbamides of the type $CS[NH\cdot C_{10}H_5(OH)\cdot SO_3H]_2$ are readily obtained by condensing a mixture of two aminonaphtholsulphonic acids with carbon disulphide and sulphur in alcoholic solution (compare this vol., i, 22). G. T. M.

Benzoylbenzylcarbamide, Benzoyl-*p*-tolylcarbamide, and the Corresponding Ethyl-*ψ*-carbamides: a Correction. By Henry L. Wheeler and Treat B. Johnson (*Amer. Chem. J.*, 1902, **27**, 218—219).—Re-examination of the substances previously described

(Abstr., 1900, i, 633—634) as benzoylbenzylcarbamide and benzoyl-*p*-tolylcarbamide, melting at 89° and 80° respectively, has shown that they are not normal but ψ-carbamides.

Benzoylbenzylethyl-ψ-carbamide (previously described as benzoylbenzylcarbamide), crystallises from alcohol in colourless prisms and melts at 89—90°; it is converted by hydrochloric acid into ethyl chloride and the true *benzoylbenzylcarbamide*, which forms colourless prisms and melts at 165—166°.

*Benzoyl-*p*-tolylethyl-ψ-carbamide* crystallises from alcohol in colourless prisms and melts at 75°; when treated with hydrochloric acid, it yields ethyl chloride and the true *benzoyl-*p*-tolylcarbamide*, which crystallises in needles and melts at 222—223°. E. G.

Phenylglycine-*o*-carboxylic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 125456. Compare Abstr., 1901, i, 710).—Phenylglycine-*o*-carboxylic acid is prepared by heating together at 220° the sodium salts of glycine and *o*-chlorobenzoic acid or its bromine analogue. G. T. M.

Action of Oxidising Agents on Pentachlorophenol. By Etienne Barral (*Bull. Soc. Chim.*, 1902, [iii], 27, 271—275).—By the action of certain oxidising agents, such as nitric acid, on pentachlorophenol, tetrachloroquinone is formed, although the conversion is in no case complete, whilst in many cases, as with chromic acid or permanganate, it is not produced. A. F.

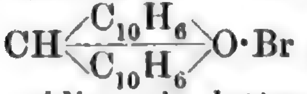
Transformation of Pentachlorophenol into Tetrachloroquinone. By Etienne Barral (*Bull. Soc. Chim.*, 1902, [iii], 27, 275—278. Compare preceding abstract).—By the action of chlorine on pentachlorophenol, heptachlorophenol is produced, and this, on heating, decomposes into hexachlorophenol and hydrogen chloride; hexachlorophenol, when acted on by oxidising agents, yields tetrachloroquinone. Since in those cases where tetrachloroquinone is produced by the action of oxidising agents on pentachlorophenol chlorine is formed, the author considers that in such cases the formation of tetrachloroquinone is due to the intermediate formation of heptachlorophenol and hexachlorophenol. A. F.

Behaviour of Picric Acid towards boiling Alkali Hydroxides. By Edgar Wedekind and J. Haeussermann (*Ber.*, 1902, 35, 1133—1135).—On boiling picric acid with excess of potassium, sodium, or barium hydroxide, ammonia is slowly evolved; after 8 hours, the evolution ceases. Approximately 5·9 per cent. of ammonia is given off, whilst $1NH_3$ requires 7·8 per cent. Prussic acid can be detected in the alkaline mother liquor together with nitrite. The amount of the latter is quantitatively different with the three alkali hydroxides; thus, from 1 gram of picric acid was obtained, with potassium hydroxide, 36·4 mg. of nitric oxide; with sodium hydroxide, 57·4 mg., and with barium hydroxide, 79·8 mg. respectively. No solid products of the reaction were isolated. K. J. P. O.

Preparation of Thymol. M. DINESMANN (D.R.-P. 125097).—2-Bromo-*p*-cymene, when treated with fuming sulphuric acid, yields a monosulphonic acid, which, on heating with zinc dust and ammonia at 170°, gives rise to a cymenesulphonic acid. This reduction product, when fused with potassium hydroxide, furnishes thymol. G. T. M.

"Halochromy" of 2 : 7-Dimethoxynaphthalene. By HUGO KAUFFMANN (*Ber.*, 1902, **35**, 1321—1324. Compare Abstr., 1900, i, 480; 1901, i, 318; and also Baeyer and Villiger, this vol., i, 380).—Dimethoxynaphthalene, when quite pure, is obtained in perfectly colourless crystals; its solution in concentrated sulphuric acid is yellow and has a well-marked, green fluorescence. A 1 per cent. solution of the ether in the concentrated acid has a reddish-brown colour similar to that of potassium dichromate, but the fluorescence is less appreciable than in more dilute solutions. These appearances are not due to a decomposition of the substance, for it is obtained quite colourless by diluting the solution with ice-cold water; the addition of glacial acetic acid, alcohol, or ether always destroys both the coloration and the fluorescence. Concentrated hydrochloric and phosphoric acids, when employed separately, do not develop any coloration with the ether, but a solution of the substance in syrupy phosphoric acid, when treated with hydrogen chloride, exhibits the same colour and fluorescence as when concentrated sulphuric acid is the solvent. The ether also exhibits intense luminescence under the influence of the Tesla radiations, and these phenomena are probably due to a tendency for the formation of a quinonoid structure in the substance under examination.

G. T. M.

The so-called Dinaphthylene Glycol. By ROBERT FOSSE (*Compt. rend.*, 1902, **134**, 663—664. Compare Abstr., 1901, i, 322, 384, 643, and this vol., i, 51, 171).—As already indicated, the supposed dinaphthylene glycol is in reality dinaphthaxanthhydrol. This view of the constitution of the substance is confirmed by the formation of the *acetyl* derivative, $OAc{\cdot}CH{<}{}^{C_{10}H_6}_{C_{10}H_6}{>}O$, by the action of acetic anhydride either on the compound itself or its anhydride, the product melting at 194°. Fuming hydrobromic acid converts the hydrol or its anhydride into bromodinaphthaxanthen, to which the constitution  $CH{<}{}^{C_{10}H_6}_{C_{10}H_6}{>}O{\cdot}Br$ is now given; this product, when treated with alcohol, oxidises the latter to aldehyde and loses hydrogen bromide, becoming itself converted into dinaphthaxanthen. G. T. M.

Solubility of Silver Benzoate. By CARL LIEBERMANN (*Ber.*, 1902, **35**, 1094).—Silver benzoate is erroneously stated in many handbooks to be soluble in 1·96 parts of absolute alcohol at 20°; this solubility is really that of benzoic acid, the silver salt being soluble only in 5910 parts of cold, and in 2150 parts of hot, alcohol. W. A. D.

Formation, Decomposition, and Germicidal Action of Benzoyl Acetyl and Diacetyl Peroxides. By PAUL C. FREER and FREDERICK G. NOVY (*Amer. Chem. J.*, 1902, **27**, 161—192).—The conditions under which benzylidene diacetate is produced by the action of acetic anhydride on benzaldehyde were investigated. The rate of action is increased by the presence of traces of acetic acid, but appears to be diminished if a large quantity is present. Metals such as platinum, zinc, tin, and iron cause a considerable acceleration. If air is passed through a carefully dried mixture of benzaldehyde and acetic anhydride, the formation of the diacetate is retarded, and benzoic acetic peroxide is produced in quantities large enough to admit of estimation.

When a solution of benzoic acetic peroxide (2 mols.) in benzaldehyde is heated, decomposition occurs with formation of carbon dioxide (2 mols.) and methane (1 mol.). This decomposition was employed for the estimation of the benzoic acetic peroxide produced in the following experiments.

Dry air was passed through a series of tubes containing a dry mixture of acetic anhydride and benzaldehyde; the amount of peroxide produced was very small, but in presence of small pieces of certain metals (particularly magnesium) or filter paper the quantity was considerably increased. The results of these experiments show that the rate of formation of the peroxide depends on the surface action of substances coming in contact simultaneously with air and the mixture of acetic anhydride and benzaldehyde; the presence of moisture is not necessary. The probable course of the reaction is discussed, and the best method of preparing the peroxide described.

Benzoic acetic peroxide melts at 40—41°. It reacts with aniline with formation of acetanilide, azoxybenzene, benzoic acid, and traces of perbenzoic acid, $C_6H_5\cdot CO\cdot O\cdot OH$. It also reacts slowly with quinol with production of quinhydrone; this action is probably due to the presence of traces of water. Although the solid peroxide does not exert an oxidising action, its aqueous solution liberates iodine from potassium iodide. This difference in behaviour was found to be due to hydrolysis, the rate of which was estimated; the results are tabulated. The hydrolysed solution yields an insoluble precipitate of benzoic peroxide and a clear liquid containing acetic and benzoic acids, peracetic acid, and some perbenzoic acid. The solubility of the peroxide at 25° was determined; in five minutes, an amount corresponding with 0·639 gram per litre was dissolved. By the action of sodium ethoxide on benzoic acetic peroxide, benzoic acid and perbenzoic acid are produced.

When acetic peroxide is treated at $-20°$ with sodium ethoxide, a white, unstable salt is produced which, when treated with frozen dilute sulphuric acid, yields an oil with an odour resembling that of chlorine oxides; this substance, which is undoubtedly peracetic acid, rapidly undergoes decomposition. Acetic peroxide, unlike benzoic acetic peroxide, when left in contact with water slowly evolves oxygen. The hydrolysis of the solution is complete in a few minutes.

The action of the peroxides on various bacterial cultures was studied; the results are tabulated. Benzoic peroxide does not exert any germicidal action, owing to the fact that it does not undergo hydrolysis in solution; the hydrolysed solutions of acetic peroxide and benzoic acetic peroxide, however, exhibit a remarkable germicidal effect. The results show that whilst the symmetrical organic peroxides are inert, the unsymmetrical per-acids are amongst the most powerful germicidal agents known. E. G.

Esterification of Acids with Phenols. By MARUSSIA BAKUNIN (*Gazzetta*, 1902, **34**, i, 178—185).—The author has studied the preparation of the phenylnitrocinnamates and phenylcinnamates of mono-, di-, and tri-hydric phenols by the action of phosphoric oxide on the acid and phenol dissolved in a neutral solvent. As the energy of the reaction increases with the number of hydroxyl groups in the phenol, a solvent of high boiling point, such as toluene, should be employed in the case of di- and tri-hydric phenols. When the latter are used in excess, they yield only mono-substituted derivatives.

o-*Tolyl phenyl*-o-*nitrocinnamate*, $C_{15}H_{10}O_3N\cdot O\cdot C_6H_4Me$, separates from alcohol in yellow, apparently rhomboidal, prisms melting at 97—98°.

o-*Tolyl phenyl*-m-*nitrocinnamate* is deposited from alcohol in crystalline granules melting at 118—120°.

o-*Tolyl* allo*phenyl*-m-*nitrocinnamate* crystallises from alcohol in tufts of silky, white needles melting at 83—84°.

o-*Tolyl phenyl*-p-*nitrocinnamate* separates from alcohol in pale yellow needles melting at 128—129°.

o-*Tolyl* allo*phenyl*-p-*nitrocinnamate*, which is obtained mixed with small quantities of phenylnitroindone, crystallised from alcohol in straw-yellow needles melting at 120°.

o-*Tolyl phenylcinnamate*, $C_{15}H_{11}O\cdot O\cdot C_6H_4Me$, separates from alcohol in silky needles melting at 130°.

2-*Methyl*-5-iso*propylphenyl phenylcinnamate*, $C_{15}H_{11}O\cdot O\cdot C_6H_3MePr^{\beta}$, is deposited from alcohol in bristly needles having a silky lustre and melting at 80—81°.

m-*Hydroxyphenyl phenylcinnamate*, $C_{15}H_{11}O\cdot O\cdot C_6H_4\cdot OH$, crystallises from alcohol in silky needles melting at 157—160°.

m-*Phenylene diphenylcinnamate*, $C_6H_4(C_{15}H_{11}O_2)_2$, obtained in small quantity mixed with the preceding compound, separates from alcohol in granules melting at 162°.

o-*Phenylene phenylcinnamate* is deposited from benzene in needles melting at 169°.

p-*Phenylene phenylcinnamate* crystallises from benzene in silky needles melting at 126—127°, and is accompanied by small quantities of a substance soluble in sodium carbonate solution and melting at 160°.

Pyrogallol phenylcinnamate, $C_{15}H_{11}O\cdot O\cdot C_6H_3(OH)_2$, separates from benzene in flocks of white needles melting at 159°. T. H. P.

Glyceryl Salicylate. ERNST TÄUBER (D.R.-P., 126311).—*Glyceryl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot C_3H_5(OH)_2$, produced by heating salicylic acid with excess of glycerol in the presence of a small quantity of 60 per cent. sulphuric acid, melts at 76°, and although sparingly soluble in cold dissolves readily in hot water. The ester is odourless, readily soluble in most organic solvents, and miscible with glycerol; it forms a compound with calcium chloride, and is readily hydrolysed by alkali hydroxides and carbonates. G. T. M.

Synthesis of β-Hydroxy-β-*p*-tolyl-αα-dimethylpropionic Acid. By I. Zeltner (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 119—128).—The action of zinc on a mixture of ethyl bromo*iso*butyrate and *p*-methylbenzaldehyde gives rise to ethyl β-hydroxy-β-*p*-tolyl-αα dimethylpropionate according to the equations: (1) $CMe_2Br{\cdot}CO_2Et + Zn = ZnBr{\cdot}CMe_2{\cdot}CO_2Et$; (2) $C_6H_4Me{\cdot}CHO + ZnBr{\cdot}CMe_2{\cdot}CO_2Et = C_6H_4Me{\cdot}CH(OZnBr){\cdot}CMe_2{\cdot}CO_2Et$;

(3) $C_6H_4Me{\cdot}CH(OZnBr)\ CMe_2{\cdot}CO_2Et + H_2O = C_6H_4Me{\cdot}CH(OH){\cdot}CMe_2{\cdot}CO_2Et + Zn(OH)Br$.

β-Hydroxy-β-p-tolyl-αα-dimethylpropionic acid, $C_6H_4Me{\cdot}CH(OH){\cdot}CMe_2{\cdot}CO_2H$, crystallises from alcohol in small prismatic needles melting at 111·5—112·5; it is soluble in water and slightly volatile in a current of steam, and gives the normal molecular weight in boiling ether. The *potassium* and *barium* salts were analysed and the *zinc*, *lead*, *nickel*, *cobalt*, *iron*, *mercury*, *silver*, and *copper* salts prepared. The *ethyl* ester is a slightly yellow, very viscous liquid boiling at 172—173° under 15 mm. pressure and having the normal molecular weight in boiling ether; n_D 1·50439 at 19°. When heated with dilute sulphuric acid, the acid is decomposed partly into carbon dioxide, water, and *iso*butenyltoluene, and partly into *iso*butyric acid and *p*-methylbenzoic acid. Heating the acid under pressure with concentrated hydriodic acid also gives rise to *iso*butenyltoluene, which is further obtained, together with *p*-methylbenzaldehyde, when the acid is submitted to dry distillation.

The acid is not obtained if the zinc be replaced by magnesium, as in this case a *compound*, $C_{11}H_{14}O_2$, separating from ether in crystals melting at 138—139° is formed, together with *p*-methylbenzaldehyde.

T. H. P.

Action of Formaldehyde on *o*-Aminobenzoic Acid in Hydrochloric Acid Solution. By Carl Goldschmidt (*Chem. Zeit.*, 1902, **26**, 179—180).—The amorphous substances obtained by Mehner (Abstr., 1901, i, 470) by the action of formaldehyde on hydrochloric acid solutions of *o*-aminobenzoic acid and methyl *o*-aminobenzoate respectively have been examined. From the acid, a substance of the formula $O(CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H)_2$, is formed, and from the ester a compound, $CH_2Cl{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Me$. These substances possess antiseptic properties.

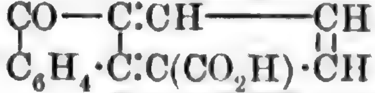
J. McC.

Polymerised Condition of ordinary Indigotin and the Transformation of Indigotin into Indirubin. By Louis Maillard (*Compt. rend.*, 1902, **134**, 470—472. Compare Abstr., 1901, ii, 407).—A mixture of indoxyl sulphate, chloroform, and concentrated hydrochloric acid develops a deep blue coloration which is far more intense than that of a saturated chloroform solution of crystallised indigotin. If the mixture is at once washed with dilute sodium hydroxide solution, the chloroform extract yields a precipitate of ordinary indigotin; but when it is allowed to remain in the presence of the acid, no precipitation occurs, the colour, however, becomes violet and finally red, and the chloroform extract on evaporation leaves a residue of indirubin. A similar phenomenon is observed when urine is treated with hydrochloric acid containing a little ferric chloride. In both cases, the "nascent" indigotin produced from the indoxyl by atmospheric oxidation appears to be far more soluble in chloroform than the crystallised variety, and changes into indirubin when allowed to remain in contact with the acid. This transformation never occurs with a solution of the crystallised substance. This difference is in all probability due to polymerisation, the "nascent" variety of indigotin having the simple indigo formula $C_{16}H_{10}O_2N_2$, whilst the crystallised modification is *bis-indigotin*, $C_{32}H_{20}O_4N_4$. This view of the molecular complexity of crystalline indigotin is confirmed by Vaubel, who found that the molecular weights of indigotin and indirubin determined by the cryoscopic method in phenol and *p*-toluidine solutions correspond with the dimeric formulæ. The "nascent" variety of indirubin has not yet been isolated. Chloroform solutions of the ordinary modification, *bis-indirubin*, in the presence of alkali hydroxides do not give rise to any trace of indigotin; it is, however, quite possible that the inverse transformation might occur with the monomeric indirubin.

G. T. M.

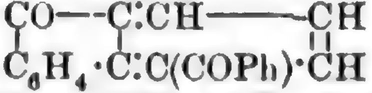
Action of Phosphorus Pentachloride on Tetrachloro-*o*-benzoylbenzoic Acid. By Léon Tétry (*Bull. Soc. Chim.*, 1902, [iii], **27**, 183—186).—On heating tetrachloro-*o*-benzoylbenzoic acid with phosphorus pentachloride in a sealed tube at 140—150° for 5 hours, as described by Kircher (Abstr., 1887, 831), the author obtained, not only tetrachloro-*o*-benzoylbenzoic chloride, but also, as the principal product, *ω-dichloro-o-benzyltetrachlorobenzoic chloride*, $CPhCl_2 \cdot C_6Cl_4 \cdot COCl$, a white, crystalline substance which melts at 143—144° and is readily soluble in benzene, toluene, or chloroform, but insoluble in alcohol. Cold concentrated sulphuric acid has no action on it, but the hot acid decomposes it with evolution of hydrogen chloride and production of a red coloration. The author has improved the yield of *o*-benzoyltetrachlorobenzoic chloride by heating *o*-benzoyl tetrachlorobenzoic acid with phosphorus pentachloride dissolved in carbon disulphide at a temperature of 30—40°. A. F.

Condensation of Diphenic Anhydride with Benzene. By Rudolf Götz (*Monatsh.*, 1902, **23**, 27—43).—On boiling a solution of diphenic anhydride in benzene with excess of aluminium chloride, 50 per cent. of *diphenyleneketonecarboxylic acid* (*fluorenone-5-carboxylic acid*),



$$\begin{array}{l} CO\text{—}C{:}CH\text{———}CH \\ C_6H_4 \cdot C{:}C(CO_2H) \cdot CH \end{array}$$

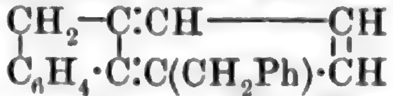
, and 10—15 per cent. of *benzoyl-5-fluorenone*,



$$\begin{array}{l} CO\text{—}C{:}CH\text{———}CH \\ C_6H_4 \cdot C{:}C(COPh) \cdot CH \end{array}$$

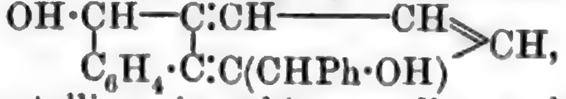
, are produced (compare Graebe and Aubin, Abstr., 1889, 145); the acid crystallises in yellow needles melting at 227°. By thionyl chloride, it is converted into *fluorenone-5-carboxylic chloride*, $C_{13}H_7O \cdot COCl$, which crystallises in long, yellow needles melting at 128°. Benzoyl-5-fluorenone, obtained as just described or by the action of aluminium chloride and benzene on fluorenone-5-carboxylic chloride, forms amber-yellow, prismatic crystals melting at 95° and boiling above 400°. The *dioxime* forms crystals melting at 215°; the *monoxime* crystals melting at 146°; the *acetyl* derivative of the latter forms small crystals melting and decomposing at 130°. The *monophenylhydrazone* of benzoyl-5-fluorenone, $C_{26}H_{18}ON_2$, crystallises in yellow needles melting at 171—173°.

On distilling benzoylfluorenone with zinc dust in a current of hydrogen, *benzyl-5-fluorene*,



$$\begin{array}{l} CH_2-C{:}CH\text{———}CH \\ C_6H_4\cdot C{:}C(CH_2Ph)\cdot CH \end{array}$$

is obtained, which crystallises in lustrous leaflets melting at 77°. When benzoylfluorenone is reduced with sodium amalgam and alcohol, or by zinc dust and acetic acid (or alcoholic ammonia), *benzhydryl-5-fluorenol*,



$$\left.\begin{array}{l} OH\cdot CH-C{:}CH\text{———}CH \\ C_6H_4\cdot C{:}C(CHPh\cdot OH) \end{array}\right> CH,$$

is formed; it crystallises in white needles melting at 145° and dissolves in concentrated sulphuric acid with an emerald green colour; the *diacetate* forms needles melting at 126°.

On reducing benzoylfluorenone with a small quantity of sodium amalgam, or by oxidising benzhydrylfluorenol with potassium permanganate, a substance is obtained which is either *benzoylfluorenol* or *benzhydrylfluorenone*; it crystallises in small, sulphur-yellow scales melting at 129°, and dissolves in concentrated sulphuric acid with a reddish-green fluorescence; the *acetate*, $C_{20}H_{13}O_2\cdot OAc$, forms pale yellow needles melting at 121°; the *phenylhydrazone*, $C_{20}H_{14}O\cdot N_2HPh$, yellow crystals melting and decomposing at 194°. K. J. P. O.

Salicylglycollic Acid. KNOLL & Co. (D.R.-P. 125988 and 125989).—Ethyl salicylglycollate (Senff, Abstr., 1881, 1127), prepared by heating sodium salicylate with ethyl chloroacetate, is readily hydrolysed by cold 25 per cent. sodium hydroxide solution by boiling for 24 hours with 50 per cent. acetic acid or by digestion at 40° with 80 per cent. sulphuric acid or 25 per cent. hydrochloric acid. *Salicylglycollic acid* crystallises from chloroform or benzene in prisms or leaflets melting at 132°; it develops a reddish-violet coloration with ferric chloride. The acid yields salicylic acid by artificial digestion or on treatment with warm solutions of the alkali hydroxides, but is not affected by gastric juice. The *sodium hydrogen* salt crystallises in needles melting at 203°; the *sodium* salt decomposes at 260°. The salts of the heavy metals are insoluble; those of calcium, strontium, and barium crystallise in needles. G. T. M.

Condensation Products from Aromatic Aldehydes and Malononitrile. By WILHELM WALTER (*Ber.*, 1902, **35**, 1320—1321).—p-*Dimethylaminobenzylidenemalononitrile*, $NMe_2\cdot C_6H_4\cdot CH{:}C(CN)_2$, produced by condensing *p*-dimethylaminobenzaldehyde with malononitrile in alcohol containing a small quantity of sodium carbonate, crystallises in orange-coloured needles and melts at 179°.

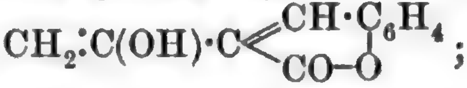
2 : 4-*Dihydroxybenzylidenemalononitrile*, $C_6H_3(OH)_2\cdot CH{:}C(CN)_2$, obtained in a similar manner from resorcinaldehyde, is sparingly soluble in alcohol or glacial acetic acid, yielding a yellow solution with a green fluorescence; it is a yellow-brown substance melting above 300°.

Isatomalononitrile, $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C{:}C(CN)_2$, obtained by mixing isatin and malononitrile in alcoholic solution, crystallises in yellowish-brown, felted needles and melts at 235°; it is soluble in hot water, alcohol, ether, benzene, or glacial acetic acid; with sodium hydroxide solution, a blue coloration is developed, and finally a yellow solution is obtained. G. T. M.

Desmotropy between Acetyl and Hydroxyvinyl Groups. By Oskar Widman (*Ber.*, 1902, **35**, 1153—1159).—Acetylcoumarin, $CAc<\begin{matrix}CH\cdot C_6H_4\\CO-O\end{matrix}$ (Knoevenagel and Amot, Abstr., 1898, i, 406), dissolves in cold *N*/10 sodium hydroxide, forming a deep yellow solution, which on heating becomes much paler in tint. The latter, less coloured, solution contains *o-hydroxybenzylideneacetoacetic acid*,

$$OH\cdot C_6H_4\cdot CH{:}CAc\cdot CO_2H,$$

which can be isolated in an impure state and begins to decompose at 118°, but is not completely melted at 160—170°. The deep yellow alkaline solution contains *hydroxyvinylcoumarin*,

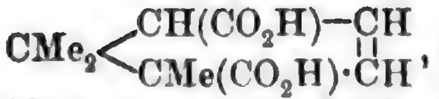


$$CH_2{:}C(OH)\cdot C<\begin{matrix}CH\cdot C_6H_4\\CO-O\end{matrix};$$

on acidification, no immediate precipitation occurs, but acetylcoumarin slowly separates as the hydroxyvinyl compound gradually undergoes isomeric change and the solution becomes neutral. Strong acids bring about an immediate separation of acetylcoumarin. The hydroxyvinyl compound can be extracted with ease by means of ether, in which it is very soluble, whereas acetylcoumarin does not dissolve particularly readily in that solvent; on the other hand, chloroform extracts the hydroxyvinyl compound from water only slowly, whilst it dissolves the acetyl derivative with great ease. With ferric chloride, an ethereal solution of hydroxyvinylcoumarin gives a yellowish-brown coloration; acetylcoumarin in ethereal solution gives no such colour. On passing dry ammonia into a solution of hydroxyvinylcoumarin in anhydrous ether or chloroform, the ammonium salt is immediately precipitated. Acetylcoumarin, when similarly treated, gives no ammonium derivative.

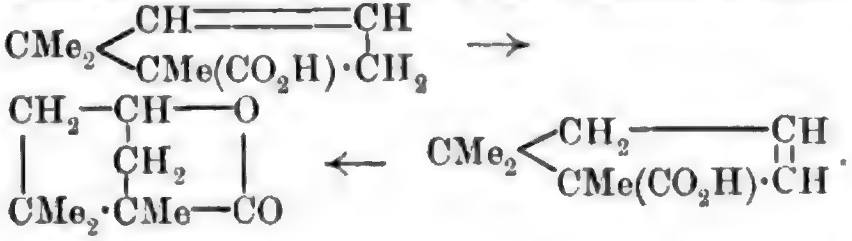
It is pointed out that the yellow, insoluble barium salt of acetylacrylic acid, described by Wolff (Abstr., 1891, 1185), is the salt of a hydroxyvinylacrylic acid, $CH<\begin{matrix}CH\cdot CO\cdot O\\C(CH_2)-O\end{matrix}>Ba$. The author finds that various ethyl alkylideneacetoacetates, on treatment with alkalis, similarly give yellow solutions, which, in the author's opinion, contain hydroxyvinyl derivatives. K. J. P. O.

Isomeric Dehydrocamphoric and Lauronolic Acids and Dihydrolaurolactone. By Julius Bredt, Jos. Houben, and Paul Levy (*Ber.*, 1902, **35**, 1286—1292).—Dehydrocamphoric acid (*Annalen*, 1898, **299**, 138), $CMe_2<\begin{matrix}C(CO_2H)=\!=CH\\CMe(CO_2H)\cdot CH_2\end{matrix}$, melts at 202—203° and does not form an anhydride. When distilled, it is partially converted into the anhydride of an *iso**dehydrocamphoric acid*, probably



$CMe_2<\begin{array}{l}CH(CO_2H)-CH\\ CMe(CO_2H)\cdot CH\end{array}$, which melts at 178—179°, whilst the anhydride melts at 182—183°. Lauronolic acid is also formed, and both the dehydrocamphoric acid and the lauronolic acid are oxidised to camphoronic acid.

The formation and reactions of these compounds are in accordance with Bredt's formula for camphor, whilst the formation from lauronolic acid and *iso*lauronolic acid of the same lactone is explained by the formulæ



T. M. L.

Hydramides and their Reactions with Ethyl Cyanoacetate.

By Lodovico Beccari (*Atti R. Accad. Sci. Torino*, 1902, **37**, 137—166).—After giving an historical account of the chemistry of the hydramides, the author gives the results of his own investigations on the reactions taking place between these substances and ethyl cyanoacetate. When these compounds are mixed in alcoholic solution in the cold, the liquid turns yellow more or less rapidly, ammonia being evolved and crystalline products formed. The nature of the latter varies in any particular case with the ratio between the amounts of hydramide and ethyl cyanoacetate employed, but the reaction always corresponds with a general scheme according to which the methylenic hydrogen of the cyanoacetate combines with either all or only part of the nitrogen, the residues then combining. In some cases, the structure of the hydramide molecule appears to be preserved, whilst in others it is destroyed.

The *compound* obtained by the interaction of hydrobenzamide (1 mol.) and ethyl cyanoacetate (2 mols.) has the constitution $CHPh:N\cdot CHPh\cdot C(CN)(CO_2Et)\cdot CHPh\cdot CH(CN)\cdot CO_2Et$, and separates from a mixture of alcohol and benzene in colourless, shining, prismatic crystals which melt and decompose at 197° and are readily soluble in benzene, less so in alcohol or ether, and insoluble in water or dilute acids or alkalis; it has a neutral reaction and gives the normal mol. weight in freezing benzene. When heated carefully at temperatures below 200°, it yields small quantities of ammonia together with ethyl α-cyano-β-phenylacrylate. It is very resistant to the action of alkalis and acids; heating with 60 per cent. potassium hydroxide solution decomposes it, but it is not attacked by boiling with concentrated hydrochloric acid; 50 per cent. sulphuric acid is without action on it, but by 70 per cent. acid it is completely decomposed into benzaldehyde, ammonia, and carbon dioxide.

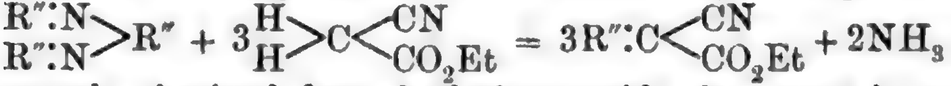
The action of excess of ethyl cyanoacetate on hydrobenzamide results in the formation of the compound $C_{22}H_{19}O_3N_3$, obtained by Carrick (Abstr., 1892, 1086) by the interaction of alcoholic ammonia and ethyl α-cyanophenylacrylate (see also Bertini, Abstr., 1901, i, 537).

Anishydramide (*p*-methoxybenzhydramide) (1 mol.) and ethyl cyanoacetate (2 mols.) yield a *compound*, $C_{34}H_{35}O_7N_3$, which has a structure analogous to that already given, and separates from alcohol in white, acicular crystals melting and decomposing at 174°; it is readily soluble in benzene, to which it gives the normal depression of freezing point. If the ethyl cyanoacetate is used in excess (4 mols.), the anishydramide molecule undergoes decomposition with the formation of ammonia and ethyl *p*-methoxyphenyl-*a*-cyanoacrylate.

Furfuramide (furfurylhydramide) (1 mol.) reacts with ethyl cyanoacetate (2 mols.), yielding ethyl furfuryl-*a*-cyanoacrylate, which is also formed when the cyanoacetate is used in excess.

The interaction of salicylhydramide (*o*-hydroxybenzhydramide) and ethyl cyanoacetate yields ethyl *o*-hydroxybenzylidenedicyanoacetate and a small quantity of another compound not yet investigated.

The final action of ethyl cyanoacetate on the hydramides, which proceeds to completion in some cases, may be represented as follows:



$$\begin{matrix}R''\!:\!N\\R''\!:\!N\end{matrix}\!\!>\!R'' + 3\begin{matrix}H\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CN\\CO_2Et\end{matrix} = 3R''\!:\!C\!<\!\!\begin{matrix}CN\\CO_2Et\end{matrix} + 2NH_3$$

; the compounds obtained from hydrobenzamide, &c., must be regarded as due to a partial scission of the hydramide, only part of the nitrogen being eliminated in the form of ammonia and replaced by one or more cyanoacetic radicles. T. H. P.

Isolation of Aldehydes. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 124229).—When a liquid containing an aldehyde is treated with a 10 per cent. solution of the barium salt of an aromatic aminocarboxylic or aminosulphonic acid, an insoluble compound is formed which on subsequent distillation in steam regenerates the aldehyde. Benzaldehyde and its homologues and derivatives, cinnamaldehyde, citral, citronellal, and salicylaldehyde may be isolated by this method. The insoluble compounds are obtained with the barium salts of naphthionic, sulphanilic, *m*-aminobenzoic, 2-hydroxy-*a*-naphthylamine-3-carboxylic, and *a*-naphthylamine-5-sulphonic acids. G. T. M.

2 : 4-Dinitrobenzaldehyde. By PAUL COHN and PAUL FRIEDLÄNDER (*Ber.*, 1902, **35**, 1265—1267).—2 : 4-Dinitrobenzyl chloride, obtained in a nearly theoretical yield by nitrating benzyl chloride, crystallises from ether in large yellow plates, melts at 34°, and is much more sensitive to alkalis than the parent substance. 2 : 4-*Dinitrobenzyl acetate* forms yellow, monoclinic plates melting at 96—97°, and 2 : 4-*dinitrobenzyl alcohol* lemon-yellow needles melting at 114—115°. 2 : 4-*Dinitrobenzylaniline* is orange-red; 2 : 4-*dinitrobenzyl*-p-*toluidine* forms slender, red needles melting at 93°; 2 : 4-*dinitrobenzyl-a-naphthylamine* dark red scales melting at 164°, and 2 : 4-*dinitrobenzylaniline*-p-*sulphonic acid* brownish-yellow needles.

2 : 4-*Dinitrobenzaldehyde* crystallises from a mixture of benzene and light petroleum in lustrous, bright yellow, rhombic plates, melts at 68—69°, and is hardly volatile with steam; on oxidation, it yields 2 : 4-dinitrobenzoic acid. 2 : 4-*Dinitrobenzylideneaniline* forms thick, orange-yellow needles; the analogous derivatives of *p*-toluidine and *a*-naphthylamine melt at 151° and 202° respectively. The *phenylhydrazone* of the aldehyde crystallises from xylene in reddish-brown

slender needles and melts at 227—228°; the *oxime* separates from water in silky needles, melts at 127—128°, and yields a *benzoyl* derivative crystallising in yellowish needles and melting at 165—166°. 2 : 4-*Dinitrobenzonitrile*, obtained by heating the oxime with acetic anhydride, forms brownish-yellow needles, melts at 104—105°, and is transformed by dilute sulphuric acid into dinitrobenzamide.

By the action of light, 2 : 4-dinitrobenzaldehyde is converted into o-*nitroso*-p-*nitrobenzoic acid*, which melts above 300° and yields a *methyl ester* crystallising in silky, yellow needles and melting at 137—138°.

W. A. D.

New Method of Preparation of Nitrobenzaldehydes. By Franz Sachs and R. Kempf (*Ber.*, 1902, **35**, 1224—1240).—Nitrosodimethylaniline undergoes condensation with di- and tri-nitrotoluenes, but not with mononitrotoluene, forming a derivative of the corresponding nitrobenzaldehyde. 2 : 4-*Dinitrobenzaldehyde*-p-*dimethylaminoanil*, $C_6H_3(NO_2)_2\cdot CH\dot{:}N\cdot C_6H_4\cdot NMe_2,H_2O$, is prepared from nitrosodimethylaniline and dinitrotoluene in alcoholic solution in presence of sodium carbonate, and crystallises in deep green needles with a metallic lustre which when rapidly heated melt at 193°. The corresponding *diethylaminoanil* melts and decomposes at about 173°. 2 : 4-*Dinitrobenzaldehyde*, $C_6H_3(NO_2)_2\cdot CHO$, is obtained by the hydrolysis of the foregoing compounds with dilute nitric acid, and crystallises in long, yellowish needles melting at 72°; it boils at 190—210° under a pressure of 10—20 mm. The *sodium hydrogen sulphite* compound crystallises in stellate groups of slender needles and is readily soluble in water. The *phenylhydrazone* is insoluble in water, crystallises in slender, dendritic needles, and melts at 232° when rapidly heated. The p-*sulphonic acid* of the phenylhydrazone crystallises in slender, reddish-yellow needles, and melts and decomposes at about 217°. 2 : 4-*Dinitrobenzaldehyde phenylbenzylhydrazone* crystallises in lustrous yellow tablets melting at 155—156°. The p-*nitrophenylhydrazone* melts and decomposes at 283—285°. All these hydrazones undergo hydrolysis with extreme difficulty.

2 : 4 : 2′ : 4′-*Tetranitrobenzalazine*, $N_2[CH\cdot C_6H_3(NO_2)_2]_2$, forms long, golden-yellow needles or rhombic crystals and melts at 246°. 2 : 4-*Dinitrobenzylideneaniline*, $C_6H_3(NO_2)_2\cdot CH\dot{:}NPh$, crystallises in light yellow needles melting at 133°. 2 : 4-*Dinitrobenzaldoxime* crystallises in long, colourless needles melting at 125°. *Nitroaminobenzaldoxime*, $NH_2\cdot C_6H_3(NO_2)\cdot CH\dot{:}N\cdot OH$, is prepared by the partial reduction of the oxime with ammonium sulphide and crystallises in matted, orange-yellow needles melting at 177—178°. It is converted by phenylhydrazine into *nitroaminobenzaldehyde phenylhydrazone*,

$$NH_2\cdot C_6H_3(NO_2)\cdot CH\dot{:}N\cdot NHPh,$$

which melts at 163°. 2 : 4-*Diaminobenzaldoxime*,

$$C_6H_3(NH_2)_2\cdot CH\dot{:}N\cdot OH,$$

is obtained by the more complete reduction of the dinitro-compound and crystallises in glistening, white plates melting at about 199—200°; it readily dissolves in dilute acids.

[With W. Everding.]—2 : 4-Dinitrobenzaldehyde may also be prepared from dinitrobenzyl chloride. This is first converted by the action of aniline into 2:4-*dinitrobenzylaniline*, $C_6H_3(NO_2)_2\cdot CH_2\cdot NHPh$, which forms golden-yellow, rectangular tablets melting at 95° (corr.). The *hydrochloride* melts at 187° (corr.), and the *picrate* at 136° (corr.). When treated in acetone solution with potassium permanganate, it is converted into 2:4-dinitrobenzylideneaniline, from which the aldehyde is obtained by hydrolysis.

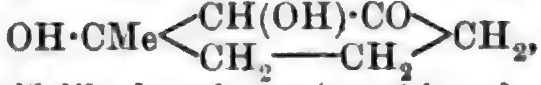
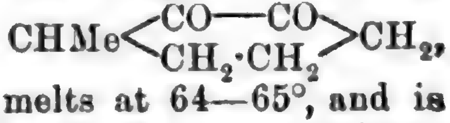
2:4:6-*Trinitrobenzaldehyde*, $C_6H_2(NO_2)_3\cdot CHO$, is prepared from trinitrotoluene and nitrosodimethylaniline, and crystallises in lancet-shaped needles melting at 119°.

[With HERM. BARSCHALL.]—*p*-Nitrobenzyl chloride condenses with nitrosodiethylaniline to form reddish-brown crystals, melting indefinitely at 154°, the composition of which has not been ascertained. On hydrolysis, this substance yields *p*-nitrobenzaldehyde and diethyl-*p*-phenylenediamine. These two compounds readily form p-*nitrobenzaldehyde*-p-*diethylaminoanil*, which closely resembles the compound just described, but melts at 142·5°. Similar results are obtained with nitrosodimethylaniline, a substance melting at 212° being formed which closely resembles the p-*nitrobenzaldehyde*-p-*dimethylaminoanil*, which melts at 217°. Some impurity must therefore be present which cannot at present be removed. A. H.

Action of Paraldehyde on *o*-Nitrosobenzoic Acid. By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1902, **35**, 1080—1081).

—*o*-Nitrosobenzoic acid in paraldehyde solution is converted slowly by bright sunlight, more rapidly by heating, into a crystalline substance, $C_9H_7O_3N$, melting at 121°, and isomeric, not identical, with *o*-nitrocinnamaldehyde. W. A. D.

A *cyclo*Ketotriose and its Conversion into Methyl-*o*-diketo-*cyclo*hexane. By CARL D. HARRIES (*Ber.*, 1902, **35**, 1176—1178).

—*Dihydroxymethyl*cyclo*hexanone*,  $\mathrm{OH\cdot CMe}{<}\begin{matrix}\mathrm{CH(OH)\cdot CO}\\ \mathrm{CH_2{-\!-\!-}CH_2}\end{matrix}{>}\mathrm{CH_2}$, obtained when methyl*cyclo*hexenone or $\Delta^{1:3}$-dihydrotoluene (see this vol., i, 361) is oxidised in aqueous acetone solution with permanganate, crystallises in cubes, melts at 52°, boils at 108—110° under 12 mm. pressure, gives a green coloration with ferric chloride, and reduces silver nitrate and Fehling's solution in the cold; the *phenylhydrazone* crystallises in small, yellowish needles, which sinter at 140° and melt at 143°, and the *semicarbazone* crystallises from water and melts and decomposes at 221—222°. When warmed with 2 mols. of phenylhydrazine, the hexanone yields a *compound* which melts at 128° and appears to be a normal osazone from which a mol. of water has been eliminated. When boiled with 5 per cent. sulphuric acid, the hexanone yields *methyl*-o-*diketo*cyclo*hexane*,  $\mathrm{CHMe}{<}\begin{matrix}\mathrm{CO{-\!-\!-}CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{CH_2}$, which crystallises from light petroleum, melts at 64—65°, and is soluble in boiling sodium hydroxide; the *diphenylhydrazone* crystallises in yellow needles and melts at 152°, whilst the *monophenylhydrazone* (?) melts at 103°; the *semicarbazones* melt respectively at 182° and 244°.

R. H. P.

Condensation of Carbon Tetrachloride with Halogen Derivatives of Benzene by means of the Friedel and Crafts Reaction. By James F. Norris and Erik H. Green (*Amer. Chem. J.*, 1901, **26**, 492—499).—4 : 4′-*Dichlorobenzophenone chloride* was obtained by the action of chlorobenzene on carbon tetrachloride in carbon disulphide solution in presence of aluminium chloride. It is a pale green, viscid liquid, distils at 217—219° (corr.) under 38 mm. pressure, and is soluble in carbon disulphide or ether, slightly so in alcohol, and insoluble in water. It dissolves in concentrated sulphuric acid with evolution of hydrogen chloride, and on dilution the ketone is precipitated.

4 : 4′-*Dichlorobenzophenone* is readily obtained from the above by boiling with dilute alcohol; it crystallises in plates, melts at 144·5°, and is easily soluble in carbon disulphide, chloroform, ether, glacial acetic acid, or acetone.

4 : 4′-*Dibromobenzophenone*, prepared in the same way from bromobenzene, melts at 171—172°, and is soluble in carbon disulphide, chloroform, benzene, or hot alcohol, but only slightly so in ether.

2 : 5 : 2′ : 5′-*Tetrachlorobenzophenone chloride*, obtained from *p*-dichlorobenzene and carbon tetrachloride in carbon disulphide solution with aluminium chloride, melts at 173—174°, is soluble in chloroform, benzene, or acetone, less so in ether, and only slightly in hot alcohol or concentrated sulphuric acid. It is converted into the corresponding ketone, 2 : 5 : 2′ : 5′-*tetrachlorobenzophenone*, by boiling with dilute alcohol; this separates from alcohol in colourless crystals which melt at 128°, and is readily soluble in hot alcohol, carbon disulphide, benzene, acetone, ethyl acetate, or chloroform.

J. McC.

Condensation of Aromatic Ketones. By R. Sorge (*Ber.*, 1902, **35**, 1065—1074).—The *semicarbazone* of cinnamylideneacetophenone, $CHPh{:}CH\cdot CH{:}CH\cdot CPh{:}N\cdot NH\cdot CO\cdot NH_2$, crystallises from ether. The corresponding *phenylhydrazone* crystallises from alcohol in brownish-yellow prisms and melts at 125—126°. By reduction with tin and alcoholic hydrogen chloride, the ketone is converted into *αε-diphenyl-α-pentanol*, $CH_2Ph\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHPh\cdot OH$, which crystallises from alcohol and melts with partial decomposition at 80—81°.

o-*Nitrobenzylideneacetophenone*, $NO_2\cdot C_6H_4\cdot CH{:}CH\cdot COPh$, crystallises from alcohol in minute, felted needles and melts at 124°; the *semicarbazone* crystallises from alcohol in minute, hair-like, felted, golden-yellow needles and melts at 177·5°; the *dibromide*, $NO_2\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot COPh$, crystallises from chloroform in short, yellowish-white, four-sided prisms, melts at 167—168°, and becomes brown and decomposes in the air.

m-*Nitrobenzylideneacetophenone* crystallises from benzene in microscopic, yellow needles and melts at 145—146°; the *dibromide* crystallises from chloroform in colourless rhombohedra, does not dissolve in ordinary solvents, and melts at 187°.

p-*Nitrobenzylideneacetophenone* crystallises from benzene in microscopic tablets and melts at 164°; the *semicarbazone* forms minute, yellow, glistening scales and melts at 178—179°; the *dibromide* crystallises from chloroform in small, slender, white prisms, melts at 148°, and slowly decomposes in air.

The *hydrazide* of *p*-tolyl methyl ketone (Claus and Wollner, Abstr., 1885, 1136), $C_6H_4Me\cdot CMe{:}N\cdot NH_2$, separates from alcohol in yellow, rhombic crystals and melts at 131—132°; the *semicarbazone* forms small, glistening, white crystals and melts at 204—205°.

Benzylidene-p-*methylacetophenone*, $CHPh{:}CH\cdot CO\cdot C_6H_4Me$, crystallises from alcohol in yellow tablets and melts at 59—60°.

Piperonylidene-p-*methylacetophenone*,

$$CH_2<{}^{O}_{O}>C_6H_3\cdot CH{:}CH\cdot CO\cdot C_6H_4Me,$$

separates from alcohol in glistening, golden crystals and melts at 130°; the *phenylhydrazone* crystallises from alcohol in yellow, prismatic tablets and melts at 135°.

The *ketone*, $CH_2<{}^{O}_{O}>C_6H_3\cdot CH{:}CH\cdot CH{:}CH\cdot CO\cdot C_6H_4Me$, crystallises from alcohol in yellowish-brown nodules and melts at 118—119°.

o-*Nitrobenzylidene*-p-*methylacetophenone*,

$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot C_6H_4Me,$$

crystallises from alcohol in minute, glistening, rectangular tablets and melts at 106—107°; the *semicarbazone*, $C_{17}H_{16}O_3N_4$, crystallises from alcohol in small, yellow, glistening, prismatic needles and melts at 111°.

m-*Nitrobenzylidene*-p-*methylacetophenone* crystallises from alcohol or carbon disulphide in hair-like, felted, yellow needles and melts at 137°; the *semicarbazone* crystallises from alcohol in hair-like needles and melts at 140°.

p-*Nitrobenzylidene* p-*methylacetophenone* crystallises from alcohol in yellow, hair-like needles and melts at 161°, the *semicarbazone* melts at 200°.

n-*Propylphenylketoxime*, $CPhPr^{a}{:}NOH$, crystallises from ether in colourless, hygroscopic needles and melts at 49—50°. The *phenylhydrazone*, $C_3H_7\cdot CPh{:}N\cdot NHPh$, is an oil; its *hydrochloride* crystallises from alcohol and melts at 199—201°. The *semicarbazone*, $C_3H_7\cdot CPh{:}N\cdot NH\cdot CO\cdot NH_2$, crystallises from alcohol in prisms and melts at 188°.

T. M. L.

Dibenzylideneacetone and Triphenylmethane. A Contribution to the Theory of Dyes. By Adolf von Baeyer and Victor Villiger (*Ber.*, 1902, **35**, 1189—1201. Compare Abstr., 1902, i, 112).—The salts of dibenzylideneacetone, which is itself colourless, are deeply coloured, a phenomenon termed by the authors *halochromism*. The production of coloured salts in this case cannot be ascribed to the acetone group itself, since the salts of dimethylpyrone are colourless, but is due to this group combined with two benzene rings. That the salts are true salts and have not a quinonoid constitution is proved by the fact that precisely similar phenomena are shown by dianisylideneacetone, in which case the salts are formed without any elimination of methyl alcohol, which would occur if they had a quinonoid constitution.

Anisylideneacetone is prepared from anisaldehyde and acetone and crystallises in long, colourless plates melting at 72—74°. It is slightly halochromic, forming a yellow solution in hydrochloric acid.

Dianisylideneacetone crystallises in long, yellow plates melting at 129—130°; it is more basic than dibenzylideneacetone, and forms more deeply coloured salts. The *sulphate*, $2C_{19}H_{18}O_3,3H_2SO_4$, crystallises in opaque, violet needles, and when treated with water yields unaltered dianisylideneacetone. The *hydrochloride* crystallises in bluish-red cubes, the *hydriodide* forms black, hair-like needles, and the *picrate* crystallises in yellowish-red, rhombic plates. It follows from the foregoing that the presence of the benzene ring in certain compounds is sufficient to render them chromophoric. Benzene itself is not halochromic, since it, like naphthalene and some other hydrocarbons, is not coloured by sulphuric acid. On the other hand, triphenylmethane forms a yellow solution in sulphuric acid, and is therefore halochromic.

The yellow colour is not due to the formation of triphenylcarbinol by oxidation, since the colour is discharged by acetic acid, whilst that of a solution of the carbinol in sulphuric acid is not affected by this reagent. It appears probable that the yellow compounds of triphenylmethyl chloride, with aluminium chloride and other negative chlorides, owe their yellow colour, not to a quinonoid constitution, but to the fact that the presence of the negative chloride converts the ester-like triphenylmethyl chloride into a true salt, in which the halochromism of the group becomes evident. This view is rendered probable by the behaviour of the more strongly basic *trianisylmethane*, $CH(C_6H_4\cdot OMe)_3$, which is prepared from anisole and anisaldehyde and crystallises in long needles melting at 45—47°. It dissolves in sulphuric acid, forming a red solution from which it is precipitated unchanged by water. The analogous amino-compound, hexamethyltriaminotriphenylmethane, on the other hand, is not halochromic. Since triphenyl-leucaniline itself is also not halochromic, it appears probable that oxonium salts may be distinguished from ammonium salts by the possession of this property, but this cannot yet be considered as definitely proved. *Trianisylcarbinol*, $C(C_6H_4\cdot OMe)_3\cdot OH$, forms large, colourless crystals melting at 83·5—84°. It behaves towards acids like triphenylcarbinol, but forms both carbonium and oxonium salts. The *chloride* is colourless, but yields coloured compounds with negative chlorides. The *nitrate* and *sulphate* are coloured and are probably true salts.

The chloride unites with hydrogen chloride to form a red oxonium salt. On decomposition, these salts yield unaltered trianisylcarbinol, so that no quinonoid change has occurred. The elimination of the methyl group, in fact, only takes place very slowly.

Dianisylphenylmethane is prepared from anisole and benzaldehyde and crystallises in needles melting at 100—100·5°. A. H.

[**1 : 8-Dihydroxynaphthaketones.**] MARTIN LANGE (D.R.-P. 126199).—1 : 8-*Dihydroxy-2-acetonaphthone*, $C_{10}H_5(OH)_2\cdot COMe$, prepared by condensing 1 : 8-dihydroxynaphthalene with glacial acetic acid in the presence of zinc chloride, melts at 100—101° and forms a *diacetyl* derivative melting at 168—169°.

1 : 8-*Dihydroxy-2-propionaphthone*, $C_{10}H_5(OH)_2\cdot COEt$, and 1 : 8-*dihydroxy-2-isobutyronaphthone*, $C_{10}H_5(OH)_2\cdot CO\cdot CHMe_2$, melt at 101—102° and 88° respectively; the *diacetyl* derivative of the latter melts at 105—106°.

1 : 8-*Dihydroxy*-2-iso*valeronaphthone*, $C_{10}H_5(OH)_2\cdot CO\cdot CH_2Pr^{\beta}$, melts at 71—72°, and its diacetyl derivative at 110—111°.

1 : 8-*Dihydroxy*-2-*benzonaphthone*, $C_{10}H_5(OH)_2\cdot COPh$, produced by condensing 1 : 8-dihydroxynaphthalene with benzoic acid, benzoyl chloride, or benzoic anhydride, melts at 121—122°; its *diacetyl* compound melts at 115—116°. These ketones crystallise from alcohol in yellow or orange-coloured needles, they condense with aromatic amines and diazonium salts, produce orange-coloured lakes with alumina, and yield an intense green precipitate with ferric chloride. G. T. M.

1 : 4-Nitroacetylaminoanthraquinone and 1 : 4-Nitroaminoanthraquinone. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 125391. Compare *Ber.*, 1882, **15**, 1790).—4-Nitro-1-acetylaminoanthraquinone, produced by treating a solution of acetyl-1-aminoanthraquinone in concentrated sulphuric acid with 20 per cent. nitric acid at 15°, crystallises from epichlorohydrin, pyridine, or glacial acetic acid in golden-yellow needles and melts at 256—258°. 4-Nitro-1-aminoanthraquinone, prepared either by performing the nitration at 90—100° or by hydrolysing the acetyl compound, crystallises from epichlorohydrin in yellowish-red needles and melts at 290—295°. G. T. M.

Polychlorodiaminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 125094).—The perchlorinated diaminoanthraquinone, consisting chiefly of *octochloro*-1 : 5-*diaminoanthraquinone*, obtained by treating 1 : 5-diaminoanthraquinone dissolved in glacial acetic acid with chlorine gas, is a yellow powder readily soluble in the ordinary organic solvents, but not in cold concentrated sulphuric acid; it sinters at 90° and melts at 100°. When treated with alkalis or reducing agents, the substance yields products, such as the penta- or tetra-chloro-derivatives, containing less chlorine. G. T. M.

Arylaminonitroanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126542).—The 1 : 5-, 1 : 7-, and 1 : 8-dinitroanthraquinones, when heated with a primary aromatic amine, exchange one of their nitro-groups for the arylamino-residue, R·NH, yielding arylaminonitroanthraquinones. Diarylaminoanthraquinones, however, are formed when the reaction is prolonged.

8-*Anilino*-1-*nitroanthraquinone* crystallises in bluish-violet needles.

7-p-*Toluidino*-1-*nitroanthraquinone*, produced from 1 : 7-dinitroanthraquinone and *p*-toluidine, crystallises from acetone in violet-black needles.

5-α-*Naphthylamino*-1-*nitroanthraquinone* crystallises from glacial acetic acid in brownish-violet needles.

These condensations are effected either by heating the reagents at 130—160°, or by mixing them together in boiling pyridine.

G. T. M.

Bromo-derivatives from Aminohydroxyanthraquinones. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126015).—When treated with bromine, the amino- or hydroxy-anthraquinones yield bromo-derivatives of the original compounds. The aminohydroxyanthraquinones, however, exchange their amidogen radicles for hydroxyl under these conditions, and are simultaneously brominated; thus, β-aminoalizarin yields bromoanthragallol (m. p. 217°), and β-aminoanthrapurpurin and β-aminoflavopurpurin similarly furnish bromohydroxyanthragallols. G. T. M.

Anthragallolsulphonic Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 125575).—*Sodium anthragallolsulphonate*, produced by boiling the bromoanthragallol from β-aminoalizarin with a concentrated solution of sodium hydrogen sulphite, crystallises on cooling in yellowish-red needles. The *acid*, prepared by using sulphurous acid instead of the sulphite, yields anthragallol when heated with sulphuric acid. G. T. M.

Conversion of Nitroanthraquinone Derivatives into the corresponding Hydroxy-compounds. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 125579).—Many nitro-compounds of the anthraquinone series, when heated with concentrated sulphuric acid containing boric acid, become converted into the corresponding hydroxy-derivatives, the nitro-group being eliminated as nitrous acid. The change is due to a specific action of the boric acid, for in the absence of this reagent the hydroxyl compound is not produced. At 80—90°, 4 : 8-dinitroanthrarufin-2 : 6-disulphonic acid is converted into 8-nitro-1:4:5-trihydroxy-2:6-anthraquinonedisulphonic acid, and at 120—150° the remaining nitro-group is removed, and 1 : 4 : 5 : 8-tetrahydroxyanthraquinone-2 : 6-disulphonic acid is obtained.

In a similar manner, 4 : 8-dinitroanthrarufin, which is not affected by sulphuric acid alone at 150°, is converted by a mixture of this reagent and boric acid first into 8-nitro-1 : 4 : 5-trihydroxyanthraquinone, and then into 1 : 4 : 5 : 8-tetrahydroxyanthraquinone.

The patent contains several other examples of this reaction and a table showing the properties of the products. G. T. M.

Variation in the Rotatory Power of the Esters of *l*-Borneol. By JULES MINGUIN and E. GRÉGOIRE DE BOLLEMONT (*Compt. rend.*, 1902, **134**, 608—610).—The authors have determined the rotatory power of a number of esters prepared from N'ghai borneol, and the results are contained in the following table. In the absence of accurate knowledge of the constitution of borneol, it is not possible to discuss the results on the basis of Guye's theory, but it is noteworthy that in the esters of the acetic series, the rotatory power is approximately inversely proportional to the molecular weight, and this holds good also for the halogen derivatives of the acids of the same series:

	Mol. wt.	Boiling point.	$[\alpha]_D$.
N'ghai borneol	154	—	−38·09°
Bornyl formate	182	215°	−49
„ acetate	196	223	−45·5
„ propionate	210	235	−42·8
„ butyrate	224	246—247	−40·01
„ *iso*butyrate	224	242—244	−40·01

	Mol. wt.	Boiling point.	$[\alpha]_D$.
Bornyl chloroacetate	230·5	263°	– 39·6°
,, valerate	238	—	– 37·4
,, dichloroacetate	265	269—270	– 29·6
,, bromoacetate	275	265	– 30·5
,, α-bromopropionate	289	271—273	– 26·8
,, trichloroacetate	299·5	276—277	– 25·7
,, α-bromo*iso*butyrate	303	150 (19 mm.)	– 27·5
,, α-bromobutyrate	303	168 (19 mm.)	– 26·4
,, trichlorobutyrate	327·5	195 (19 mm.)	– 20·5
,, laurate	336	250 (40 mm.)	– 27·7
,, αα-dibromopropionate	368	190 (20 mm.)	– 20·2
,, tribromoacetate	433	m. p. 61	– 19·03

C. H. B.

Basic Properties of Quadrivalent Oxygen. By OTTO SACKUR (*Ber.*, 1902, **35**, 1242—1252).—Measurements of the conductivity of solutions of cineol in hydrochloric acid show that cineol hydrochloride is completely dissociated hydrolytically into acid and base. The basicity of cineol is, however, proved by the fact that its solubility in dilute acids is greater than in pure water, the solubility increasing with the concentration of the acid ; a similar method has already been applied to ethyl ether (compare Jüttner, Abstr., 1901, ii, 595). Another proof is given by the fact that the diminution of the solubility in water of cineol, caused by the presence of a base such as potassium or sodium hydroxide, is much greater than that due to a neutral salt such as sodium chloride.

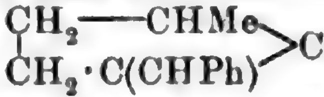
Measurements are given showing that the molecular conductivity of dry hydrogen chloride in ether, amyl alcohol, or cinnamaldehyde, diminishes with increasing dilution, a fact indicating the basic nature of these substances ; with aniline and *o*-toluidine, similar observations were made, but with nitrobenzene, benzaldehyde, and acetone, which must be considered non-basic in character, an increase in conductivity was observed.

A discussion of the nature of the salts of dimethylpyrone and of the basicity of cinnamaldehyde closes the paper. W. A. D.

Oxidation of Menthone, Pulegone, and β-Methylhexanone. By NICOLAI A. SPERANSKY (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 10—17).—Various investigators have ascribed different melting points to β-methyladipic acid obtained by the oxidation of menthone, pulegone, and β-methylhexanone, reactions which the author has now examined.

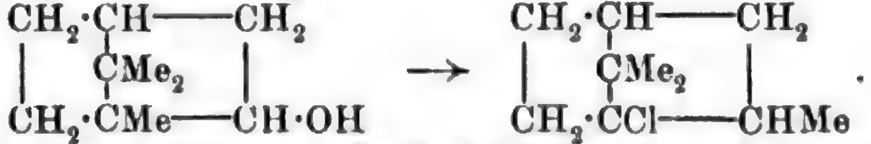
Whether oxidised by potassium permanganate or by concentrated or dilute nitric acid, methylhexanone yields only β-methyladipic acid melting at 67°. This was shown by the action of benzaldehyde on the acid obtained, which yielded only dibenzylidene-β-methylpentanone and no monobenzylidene-α-methylpentanone, as should be the case if any α-methyladipic acid were present.

The β-methyladipic acid obtained by the oxidation of pulegone with permanganate is found to contain a certain quantity of its anhydride, which with aniline forms an *anilino-acid*, $C_{13}H_{17}O_3N$, separating from ether in crystals melting at 120°. The β-methyladipic acid free from anhydride melts at 91° and has $[\alpha]_D$ $+8°38'$. The acid obtained from menthone melts at 84°, has $[\alpha]_D$ $+9°48'$ and with benzaldehyde gives dibenzylidene-β-methylpentanone; it is probable that there is anhydride present in this acid but this has not been confirmed.

Benzylidene-α-methylpentanone,  $\begin{array}{l}CH_2\text{——}CHMe\\ CH_2\cdot C(CHPh)\end{array}\!\!>\!CO$, obtained by the condensation of benzaldehyde with α-methylpentanone, separates from a mixture of ether and light petroleum in bundles of long, silky, white crystals melting at 123—124°; it is readily soluble in ether or ethyl acetate and is coloured brown by strong sulphuric acid.

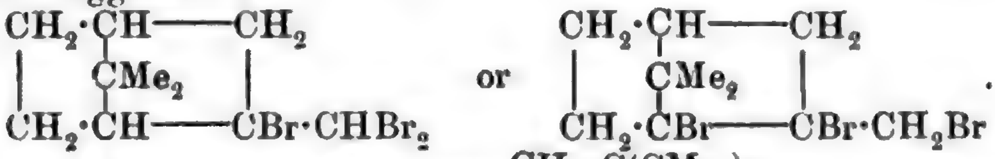
T. H. P.

Camphene and Camphor. By Friedrich W. Semmler (*Ber.*, 1902, **35**, 1016—1022. Compare Abstr., 1901, i, 90).—It is suggested that the formation of *iso*bornyl chloride by the action of phosphorus pentachloride on borneol is due to an isomeric change of the Beckmann type; the formulæ given are:

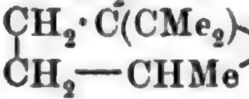


$$\begin{array}{l}CH_2\cdot CH\text{——}CH_2\\ |\qquad CMe_2\qquad |\\ CH_2\cdot CMe\text{——}CH\cdot OH\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CH\text{——}CH_2\\ |\qquad CMe_2\qquad |\\ CH_2\cdot CCl\text{——}CHMe\end{array}.$$

Bromocamphene dibromide, $C_{10}H_{15}Br,Br_2$, prepared by the action of bromine on bromocamphene, crystallises from alcohol, melts at 77—78°, and is inactive. *Chlorocamphene dichloride*, $C_{10}H_{15}Cl,Cl_2$, boils at 130—135° under 10 mm. pressure and melts at 135°. The formula suggested is



$$\begin{array}{l}CH_2\cdot CH\text{——}CH_2\\ |\qquad CMe_2\qquad |\\ CH_2\cdot CH\text{——}CBr\cdot CHBr_2\end{array} \quad\text{or}\quad \begin{array}{l}CH_2\cdot CH\text{——}CH_2\\ |\qquad CMe_2\qquad |\\ CH_2\cdot CBr\text{——}CBr\cdot CH_2Br\end{array}.$$

The formula of camphorphorone,  $\begin{array}{l}CH_2\cdot C(CMe_2)\\ CH_2\text{——}CHMe\end{array}\!\!>\!CO$, previously suggested (*Ber.*, 1892, **25**, 3520) is confirmed by experiments on the reduction and subsequent oxidation of the compound, but details are not yet given.

T. M. L.

Camphidone and Camphidine. C. F. Boehringer & Söhne (D.R.-P. 126196).—*Camphidone*, $C_{10}H_{17}ON$, produced by electrolysing in the cathode cell a solution of camphorimide in 65 per cent. sulphuric acid, is isolated by partly neutralising the product with calcium carbonate and extracting the solution with chloroform; it melts at 220°, boils at 308°, and is soluble in all the ordinary solvents with the exception of cold water; its picrate crystallises in yellow needles. *Camphidine*, $C_{10}H_{19}N$, is obtained from the mother liquors in the preceding reduction by adding excess of alkali hydroxide and distilling in steam; it is a soft, white, crystalline substance, melting at 188° and boiling at 209°.

G. T. M.

***cyclo*Citral.** Haarmann & Reimer (D.R.-P. 123747).—Citral, when condensed with aniline and ethylamine, yields citralideneaniline and citralidene-ethylamine respectively; these substances are oils. When slowly added to cold concentrated sulphuric acid, they give rise to products which, when diluted with water and distilled in steam, furnish *cyclo*citral. The crude cyclic aldehyde boils at 85—100° under 16 mm. pressure, and when purified by means of its semicarbazone yields β-*cyclo*citral. Phosphoric acid may be employed to bring about the transformation, and in this case the mixture is gently warmed.

G. T. M.

Synthesis in the Terpene Series by Means of Haloid Compounds of Aluminium. By MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 31—33).—*Phenyldihydropinene*, $C_{10}H_{17}Ph$, prepared by the interaction of carefully dried pinene hydrochloride and benzene in presence of aluminium chloride, boils at 286—291° under 745 mm. pressure and has the normal molecular weight in freezing benzene; it has the sp. gr. 0·9594 at 20°/0° and n_D 1·52691 at 20°. The hydrocarbon exhibits the usual characters of saturated compounds and reacts vigorously with dilute nitric acid. T. H. P.

Proximate Analysis of the Essence of Mentha Pulegium. By LÉON TÉTRY (*Bull. Soc. Chim.*, 1902, [iii], **27**, 186—193. Compare Abstr., 1891, 936).—From essence of Polei, by fractional distillation under 20 mm. pressure, the author obtained three fractions boiling below 105°, between 105° and 110°, and between 110° and 112° respectively. The last fraction consists chiefly of pulegone, but also contains menthol (about 10 per cent.) and possibly also α- or β-*iso*pulegone. The lower boiling fractions contain menthone and probably some terpenes, but the latter could not be sufficiently characterised.

A. F.

Essence of Sweet Orange Blossom or Neroli Portugal. By EUGÈNE THEULIER (*Bull. Soc. Chim.*, 1902, [iii], **27**, 278—280).—When obtained by the simple distillation of the blossoms, the essence forms a dark yellow liquid, the odour of which does not at all resemble that of the ordinary oil of neroli. The author has discovered the presence in it of *d*-camphene, *d*-limonene, and of *d*-linalool, but owing to the loss of a considerable portion, the examination of the oil is incomplete. The presence of methyl anthranilate could not be detected. On cooling the essence, crystalline lamellæ are obtained, which melt at 55° and readily volatilise without decomposition. A. F.

Behaviour of Crude Caoutchouc towards Concentrated Nitric Acid. By RUDOLF DITTMAR (*Ber.*, 1902, **35**, 1401—1402. Compare Harries, Abstr., 1901, i, 733).—Crude caoutchouc is vigorously attacked by concentrated nitric acid and yields a yellowish-red substance, which is purified by repeated precipitation of its solution in ethyl acetate by ether; it begins to decompose at 142—143°, is readily soluble in alkalis, forming a blood-red solution. Analysis and a molecular weight determination show that it has the formula $C_{10}H_{12}O_6N_2$, and on titration with sodium hydroxide and phenolphthalein it behaves as a monobasic acid. K. J. P. O.

Saponarin, a New Glucoside from Saponaria. By GEORGE BARGER (*Ber.*, 1902, **35**, 1296—1298).—Saponarin dissolves in about 1000 parts of hot water and crystallises on cooling in minute, birefringent needles. It dissolves in alkalis with an intense yellow colour, and gives a blue colour with a solution of iodine in potassium iodide; the blue colour is destroyed by large excess of water, by alcohol, ether, or chloroform and by warming. It gives a brownish-red colour with ferric chloride, a yellow precipitate with lead acetate, and a white precipitate with silver nitrate. It contains C = 50·66, H = 6·30, loses water in a vacuum or at 100°, and when dry is very hygroscopic. It is hydrolysed by mineral acids with formation of dextrose, and a substance which still reacts like saponarin, but gives no blue coloration with iodine; *p*-hydroxybenzoic acid was isolated from the product, together with an aromatic alcohol, probably quinol. Saponarin resembles Molisch and Goldschmiedt's scutellarin (this vol., i, 48) and is perhaps the glucoside of a flavone derivative.

T. M. L.

Artemisin. By PAUL HORST (*Chem. Zeit.*, 1902, **26**, 203).—Artemisin ($C_{15}H_{18}O_4$), on oxidation with potassium permanganate, gives *artemic acid*, $C_{14}H_{16}O_4$, which forms prismatic, colourless crystals, melts at 179—181°, and is readily soluble in alcohol, but only sparingly so in water or ether.

J. McC.

Theory of Dyeing. By EDMUND KNECHT (*Ber.*, 1902, **35**, 1022—1024).—Silk dyed with "night-blue" can be completely decolorised by extraction with alcohol; when the alcoholic extract is poured into baryta-water, the colour-base is precipitated, but the solution, when filtered and precipitated with carbon dioxide, gives a coloured precipitate when treated again with "night-blue" or with magenta. This behaviour is explained by supposing that the base combines with a compound similar to sericic acid, forming a lake insoluble in water but soluble in alcohol, which therefore extracts from the fibre the acid constituent as well as the basic dye.

T. M. L.

Chlorophyll. By LEO MARCHLEWSKI (*J. pr. Chem.*, 1902, [ii], **65**, 161—167).—A mixture of the imide and anhydride of hæmatic acid is obtained when phylloporphyrin is oxidised with potassium chromate in acetic acid solution (see Abstr., 1901, i, 298). The product obtained by the reduction of phyllocyanin with zinc dust is identical with the hæmopyrrole previously obtained by the author and Nencki (Abstr., 1901, i, 554).

Phylloporphyrin is a fairly strong base, the salts of which give absorption spectra quite different to that of the base itself, and comparison of the spectra given by very dilute aqueous solutions of the base and of the salts leads to the conclusion that practically no hydrolytic dissociation has occurred with the latter. As, however, all the salts in very dilute solutions of equal molecular strength give identical spectra, it must be assumed that electrolytic dissociation has taken place, and that the spectrum is that of the coloured positive ion $C_{16}H_{19}ON_2$.

R. H. P.

Bile-pigments. By WILLIAM KÜSTER (*Ber.*, 1902, **35**, 1268—1278).—The pigments isolated from gall-stones are not necessarily present as such, but may have been formed during the process of extraction. The fraction soluble in chloroform contains at least two substances; bilirubin is soluble in 600 parts of chloroform, but is accompanied by a brownish-green pigment which contains less nitrogen, dissolves in 30 parts of chloroform, dissolves readily in dimethylaniline, but does not separate well on cooling and is soluble in alkalis to a deep red liquid. To free the bilirubin from this substance, it must be repeatedly extracted with chloroform; the product is then separated from bilirubin by extraction with alcohol, and when dissolved in hot dimethylaniline separates on cooling in beautiful crystals having the composition $C_{16}H_{18}N_2O_3$. Bilirubin is appreciably soluble in ethyl benzoate and dissolves in 30 parts of *iso*amyl benzoate, half of the substance separating on cooling in indistinct crystals.

A summary is given of the results which have been obtained in establishing a relationship between the bile and blood pigments and especially between the isomeric bilirubin and hæmatoporphyrin. T. M. L.

δ-Nitropyromucic Acid. By HENRY B. HILL and GEORGE R. WHITE (*Amer. Chem. J.*, 1902, **27**, 193—205).—By the action of nitric acid on δ-sulphopyromucic acid, δ-nitropyromucic acid, dinitrofurfuran, and nitrofurfuransulphonic acid are produced. If nitric acid is allowed to act on a solution of pyromucic acid in fuming sulphuric acid, nitropyromucic acid and dinitrofurfuran are obtained, but no nitrofurfuransulphonic acid can be isolated.

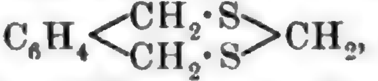
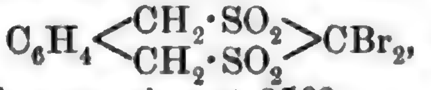
Potassium nitrofurfuransulphonate crystallises in rectangular prisms; when treated with concentrated nitric acid, it yields dinitrofurfuran. If the salt is heated with hydrobromic acid at 100° in a sealed tube, hydroxylamine, sulphuric acid, and an acid (probably bromosuccinic) melting at 160—161° are produced.

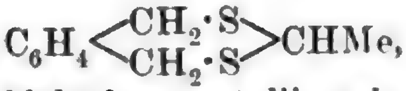
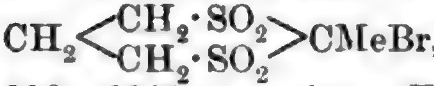
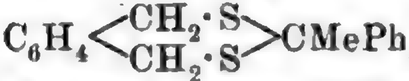
αα-Dinitrofurfuran, first obtained by Hill and Palmer (Abstr., 1889, 37), crystallises from alcohol in pale yellow, slender prisms, melts at 101°, and sublimes at a lower temperature; it is soluble in ether, benzene, hot alcohol, or hot chloroform and is volatile with steam. It is readily attacked by barium hydroxide with formation of barium nitrite and maleate.

Aniline δ-nitropyromucate crystallises in colourless leaflets. If aniline hydrochloride is added to nitropyromucic acid dissolved in solution of sodium acetate, carbon dioxide is evolved and a red precipitate is produced which consists of a mixture of two substances, one of which is yellow and the other crimson. The yellow *substance*, $C_{16}H_{13}ON_3$, forms stellate groups of rectangular crystals, melts at 232°, and is soluble in glacial acetic acid; on reduction with zinc dust and acetic acid, it yields succinanil, aniline, and ammonia. The crimson *substance*, $C_{17}H_{13}O_3N_3$, crystallises from hot glacial acetic acid in flat needles, melts and decomposes at 218°, and is readily soluble in chloroform or benzene.

Corresponding compounds were obtained from *p*-toluidine. The yellow *substance*, $C_{18}H_{17}ON_3$, crystallises from glacial acetic acid in groups of prisms and melts at 250°; on reduction, it yields ammonia, *p*-toluidine, and a substance melting at 153—154° which is probably a-tolylsuccinimide. The crimson *compound*, $C_{19}H_{17}O_3N_3$, crystallises from glacial acetic acid in needles and decomposes on heating.

E. G.

Cyclic Compounds containing Sulphur. By WILHELM AUTENRIETH and R. HENNINGS (*Ber.*, 1902, **35**, 1388—1400. Compare Abstr., 1901, i, 560).—To *o*-xylylene mercaptan and formaldehyde in solution in mol. proportions are added a few drops of concentrated hydrochloric acid; a reaction takes place, with the formation of *cyclo-o-xylylene-1 : 3-dithio-2-methylene*,  $C_6H_4{<}\begin{matrix}CH_2\cdot S\\ CH_2\cdot S\end{matrix}{>}CH_2$, which crystallises in prisms melting at 152—153°; on oxidation with acid potassium permanganate, the corresponding *disulphone* is obtained crystallising in prisms melting above 300°, and is soluble in alkali hydroxides and carbonates. When boiled with bromine water, a *dibromide*,  $C_6H_4{<}\begin{matrix}CH_2\cdot SO_2\\ CH_2\cdot SO_2\end{matrix}{>}CBr_2$, is produced; it forms prisms melting and decomposing at 250°.

cyclo-o-*Xylylene-1 : 3-dithio-2-methylmethylene*,  $C_6H_4{<}\begin{matrix}CH_2\cdot S\\ CH_2\cdot S\end{matrix}{>}CHMe$, prepared from *o*-xylylene mercaptan and acetaldehyde, crystallises in needles melting at 110° and yields, on oxidation, a *disulphone* which forms lustrous leaflets melting and decomposing above 300°; with bromine water, the disulphone gives a *monobromide* which melts and decomposes at 250°. It is found that *cyclo*-2-methyltetramethylene-1 : 3-disulphone, when treated with bromine water, yields a *bromide*,  $CH_2{<}\begin{matrix}CH_2\cdot SO_2\\ CH_2\cdot SO_2\end{matrix}{>}CMeBr$, which crystallises in long needles melting at 208—210°. cyclo-o-*Xylylene-1 : 3-dithio-2-phenyl-2-methylmethylene*  $C_6H_4{<}\begin{matrix}CH_2\cdot S\\ CH_2\cdot S\end{matrix}{>}CMePh$, prepared from *o*-xylylene mercaptan and acetophenone, melts at 126° and is oxidised to a *disulphone* which crystallises in leaflets melting at 202°.

o-*Xylylenedibenzyldisulphone*, $C_6H_4(CH_2\cdot SO_2\cdot C_7H_7)_2$, is obtained from *o*-xylylenedibenzylthio ether, which is prepared by mixing in alcoholic solution *o*-xylylene mercaptan, benzyl chloride, and sodium ethoxide; the disulphone crystallises in needles melting at 195°.

m-*Benzenedisulphoneanilide*, $C_6H_4(SO_2\cdot NHPh)_2$, prepared from *m*-benzenedisulphonic chloride and aniline, crystallises in needles melting at 143° and soluble in alkali hydroxides and carbonates; *dibenzyl*-m-*benzenedisulphonanilide*, $C_6H_4(SO_2\cdot NPh\cdot C_7H_7)_2$, obtained by boiling a solution of the anilide and sodium ethoxide in alcohol with excess of benzyl chloride, crystallises in needles melting at 170°; the *diacetyl* derivative, prepared from the anilide and acetic anhydride, forms prisms melting at 171°. Neither by the action of iodine on the mercury or silver salts of the sulphoneanilide, nor by the action of methylene iodide or ethylene bromide on the sodium salt, could the formation of a ring be induced.

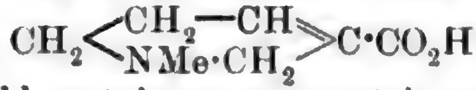
m-*Phenylene-di-iodomethyldisulphone*, $C_6H_4(SO_2\cdot CH_2I)_2$, is obtained by heating potassium *m*-benzenedisulphinate and methylene iodide under pressure at 150° and crystallises in leaflets melting at 263—265°.

On acidifying with dilute sulphuric acid, a solution containing equivalent quantities of potassium *m*-benzenedisulphinate and sodium nitrite, m-*benzenedisulphonehydroxamic acid* (m-*benzenedisulphonehydroxylamine*), $C_6H_4\vdots(SO_2)_2\vdots N\cdot OH$, is formed; it crystallises in white needles decomposing at 215°, is soluble in alkali hydroxides and carbonates, and is easily hydrolysed by boiling water to the disulphinic acid and nitrous acid.

m-*Phenylenedibenzyldisulphone*, $C_6H_4(SO_2\cdot C_7H_7)_2$, prepared from potassium *m*-benzenedisulphinate and benzyl chloride in the presence of alcohol, crystallises in lustrous leaflets melting at 240°.

It is shown that the disulphones herein described are not hydrolysed by boiling alkali hydroxides; only β-disulphones, in which the two sulphone groups are attached to neighbouring carbon atoms, can thus be hydrolysed. K. J. P. O.

Extraction of Alkaloids from Alkaline Liquids. By EDMUND SPRINGER (*Chem. Centr.*, 1902, i, 528; from *Pharm. Zeit.*, **47**, 82—83).—Alkaloids may be conveniently extracted from liquids in which they are partly dissolved and partly suspended, by using chloroform in a "perforation apparatus"; every trace of the alkaloid is dissolved by this means. Morphine, however, which is not readily soluble in pure chloroform, is an exception, and may be more completely extracted by precipitating with ammonia and using a mixture of chloroform with 10 per cent. of alcohol. An excess of alkali is to be avoided in the case of some alkaloids, such as veratrine and codeine. E. W. W.

Arecoline and Arecaidine. By HANS MEYER (*Monatsh.*, 1902, **23**, 22—28).—From the fact that the arecaidine occurring naturally is optically inactive, and that neither synthetical arecaidine nor its methyl ester (arecoline) can be resolved, it is concluded that it is 1-methyl-Δ^3-tetrahydronicotinic acid,  $CH_2<\begin{matrix}CH_2—CH\\NMe\cdot CH_2\end{matrix}>C\cdot CO_2H$, and not the Δ^4-tetrahydro-acid, which would contain an asymmetric carbon atom. Further, whilst $\beta\gamma$-unsaturated acids are converted into $\alpha\beta$-saturated acids by boiling with concentrated alkali hydroxide, arecaidine undergoes no change. K. J. P. O.

Formation of Tropine from Tropidine and Synthesis of Atropine. By ALBERT LADENBURG (*Ber.*, 1902, **35**, 1159—1162).—Details are given of the author's method (Abstr., 1890, 1333) for converting tropidine into tropine by means of hydrogen bromide, a method which has been rejected as unworkable by Willstätter (Abstr., 1901, i, 223). The separation of tropine from ψ-tropine is best effected by transformation of the bases into the aurichlorides, the tropine salt being then obtained by crystallisation from hot water. The steps in the complete synthesis of atropine are tabulated. R. H. P.

Conium Alkaloids. By FELIX B. AHRENS (*Ber.*, 1902, **35**, 1330—1334).—A mixture of bases obtained as a residue in the manufacture of *d*-coniine was found to consist principally of *l*-1-*methylconiine* and *d*-coniine. These were separated by means of the hydrobromides, *d*-coniine hydrobromide being much the less soluble.

l-*Methyl*-1-*coniine* is a colourless liquid with an odour like coniine, boils at 175·6° under 767 mm. pressure, has a sp. gr. 0·8349 at 20°/20°, and $[\alpha]_D$ −81·92° at 20°. The *hydrochloride* crystallises in needles melting at 191—192°; the *hydrobromide* crystallises from water in large needles, or from alcohol in leaflets melting at 189—190°, and the *hydriodide* in small, lustrous leaflets melting at 147°. The *platinichloride* separates from water in clusters of orange-coloured crystals and melts at 153—154°; the *aurichloride* crystallises in small, lustrous leaflets melting at 77—78°. The *mercurichloride*, $C_9H_{19}N,HCl,3HgCl_2$, separates from water in transparent crystals which melt at 152—153°, and the *picrate* in long needles which melt at 121—122°.

The coniine may be more readily separated from the methylconiine by transformation into the nitroso-compound. The coniine obtained from the nitroso-compound is a mixture of *d*- and *i*-coniine, from which the *d*-coniine can be separated by means of its hydrogen tartrate. The *l*-coniine thus obtained boiled at 166·5° and had α_D −15° at 20°. The *hydrochloride* crystallises in needles melting at 214—215°; the *hydrobromide* in silky needles melting at 205°; the *hydriodide* in needles melting at 145—146°, and the *nitrate* in needles melting at 82—83°. The *platinichloride* separates from water in red crystals melting at 160°, and the *aurichloride* in long, golden-yellow prisms melting at 59°. The coniine obtained by treatment of the methylconiine with hydrogen iodide is partially racemised. R. H. P.

Corydalis Alkaloids. By JOHANNES GADAMER [with H. ZIEGENBEIN and H. WAGNER] (*Arch. Pharm.*, 1902, **240**, 81—113. Compare this vol., i, 306).—Corycavine (Freund and Josephy, Abstr., 1892, 1367; Ziegenbein, Abstr., 1897, i, 176) gave numbers on analysis which agree best with the formula $C_{23}H_{23}O_8N$; it is optically inactive.

Corycavamine, $C_{21}H_{21}O_5N$, does not contain methoxyl or hydroxyl groups; it melts at 147—148° and has $[\alpha]_D$ +166·6° in 2·23 per cent. chloroform solution at 20°. It is a monoacid base; the *hydrochloride*, *hydrobromide*, *hydriodide*, *sulphate* (with $6H_2O$), *nitrate*, *aurichloride*, and *platinichloride* were analysed. When it is heated at 180° for a few minutes and the product crystallised from alcohol, it is converted into an optically inactive isomeride, i-*corycavamine* melting at 213—214°; this is certainly not identical with crytopine.

Bulbocapnine, which contains a methoxyl group and forms a triacetyl derivative (Ziegenbein, Abstr., 1897, i, 175; Herzig and Meyer, Abstr., 1898, i, 53), could not be made to yield a tetramethoxy-compound by boiling this derivative with methyl alcoholic sodium methoxide; some other product was obtained. By oxidising it with ½ per cent. aqueous potassium permanganate, a small quantity of a crystalline product was obtained.

Corydine (compare Merck, Abstr., 1893, i, 492), $C_{21}H_{23}O_4N$ (or $C_{21}H_{25}O_4N$), contains two methoxyl groups and reacts with acetic anhydride, yielding a product which melts at 112°, but when analysed gives numbers difficult of interpretation. It melts at 129—130° when crystallised from ether; from dilute alcohol, it was once obtained in needles which melted and decomposed at 103—105° and probably contained water or alcohol of crystallisation. It has $[\alpha]_D$ +204·3° in 1·56 per cent. chloroform solution at 20°. It is a monoacid base; the *hydrochloride*, *hydrobromide*, and *nitrate* were analysed.

Corytuberine (Dobbie and Lauder, Trans., 1893, **63**, 485) can be obtained in considerable quantity from the tubers by concentrating the extract after it has been exhausted with ether, making the residue slightly alkaline with ammonia, adding a little chloroform, and shaking; an amorphous deposit is formed which becomes crystalline after a time. The analyses agree best with the formula $C_{19}H_{23}O_4N,5H_2O$, or $C_{17}H_{15}N(OMe)_2(OH)_2$, since two hydroxyl groups are present in addition to the two methoxyl groups. It melts and decomposes at 240° and has $[\alpha]_D$ +282·6° in 0·198 per cent. alcoholic solution at 20°. It is a monoacid base; the *hydrochloride* (with $[\alpha]_D$ 167·7° in 1·99 per cent. solution), *hydrobromide*, *sulphate* (with $4H_2O$), and *platinichloride* (with $3H_2O$) were analysed; the aurichloride is very unstable. The *diacetyl* derivative crystallises from absolute alcohol with $1C_2H_5{\cdot}OH$ and melts at 72°; its *platinichloride* was analysed; its *aurichloride* melts at 195—196°. When corytuberine is heated with methyl alcoholic methyl iodide at 95°, it forms a crystalline compound which melts above 250°, but no base could be obtained from this. C. F. B.

Decomposition Products of *d*-Lupanine from Lupinus Albus.

By Arturo Soldaini (*Chem. Centr.*, 1902, i, 669; from *Boll. Chim. Farm.*, **41**, 37—46).—The original paper contains a description of methods of separating the bases still contained in (? crude) *d*-lupanine. In addition to the bases $C_8H_{15}ON$ and $C_7H_{11}ON$, the presence of at least one other base seems to have been proved. These substances are soluble in cold water, strongly alkaline and odourless, but when treated with potassium hydroxide and a small quantity of water they all emit very similar odours. E. W. W.

Quinine and Cinchonidine Ethyl Carbonates.

Vereinigte Chininfabriken Zimmer & Co. (D.R.-P. 123748. Compare Abstr., 1901, i, 738, 739).—Quinine ethyl carbonate is produced by heating together crystallised quinine hydrochloride, ethyl chloroformate, pyridine, and benzene. Cinchonidine ethyl carbonate is obtained in a similar manner from cinchonidine hydrochloride. G. T. M.

Double Dissociation.

By Edgar Wedekind and Robert Oechslen (*Ber.*, 1902, **35**, 1075—1080. Compare this vol., i, 277).—The following results show that "double dissociation" only occurs in the case of quaternary bases containing a methyl group, and is therefore probably due to the "mobility" of the latter; when a hydrogen atom is present instead of a methyl radicle, the same change occurs still more readily.

Ethyl 1-benzylpiperidiniumiodoacetate (this vol., i, 233), when heated at 193—194°, decomposes without yielding a definite product; ethyl iodoacetate is not formed. *Ethyl* 1-*methylpiperidiniumiodo-*

acetate, $C_5NH_{10}MeI\cdot CH_2\cdot CO_2Et$, on the other hand, which separates from alcohol in colourless crystals and melts at 158—159°, decomposes at 175°, giving dimethylpiperidinium iodide and ethyl iodoacetate.

Ethyl 1-*ethyltetrahydroquinoliniumiodoacetate* forms slightly yellow crystals and decomposes at 128—130° without yielding a definite product; it thus differs from the corresponding methyl derivative. Whereas ethyl 1-methyltetrahydro*iso*quinoliniumiodoacetate decomposes at 160°, forming dimethyltetrahydro*iso*quinolinium iodide, the analogous ethyl compound decomposes at 110° without yielding a crystalline product; the same is true of *ethyl* 1-*benzyltetrahydro*iso*quinoliniumiodoacetate*, which crystallises from acetone and decomposes at 154—155°.

Ethyl tetrahydroquinolineacetate hydrochloride,

$$C_9NH_{10}\cdot CH_2\cdot CO_2Et,HCl,$$

crystallises in leaflets, sinters at 90°, melts and decomposes at 95—97°, and is so prone to double dissociation that it is transformed by recrystallisation from absolute alcohol or chloroform into tetrahydroquinoline hydrochloride; by water at 0°, it is hydrolysed into hydrochloric acid and ethyl tetrahydroquinolineacetate. W. A. D.

Compounds of Thallic Chloride with Organic Bases. By Carl Renz (*Ber.*, 1902, **35**, 1110—1115).—Thallic chloride forms additive compounds with organic bases when alcoholic solutions of the metallic salt and the base are mixed, and also double salts with the hydrochlorides of organic bases, which are prepared from solutions of the base and thallic chloride in hydrochloric acid, or by treatment of the additive compounds just mentioned with hydrochloric acid. Both classes of derivatives crystallise well and are not hygroscopic; water decomposes the additive compounds far more easily than the double salts. The double chlorides are converted into corresponding bromides and iodides by treatment with potassium bromide and iodide respectively. The following substances are described: with pyridine, the *thallichloride*, $TlCl_3,(C_5NH_5)_3$, and *thalliiodide*, TlI_3,C_5NH_5; and the *double* salts $(TlCl_3)_2(C_5NH_5,HCl)_3$, melting at 130°, and $(TlI_3)_2,(C_5NH_5,HI)_3$; with quinoline, the *thallichloride*, $TlCl_3,(C_9NH_7)_3$, and the *double* salts, $TlCl_3,(C_9NH_7,HCl)_2$ and $TlI_3,(C_9NH_7,HI)_2$. The *double* salt of thallic chloride and camphylamine hydrochloride, $TlCl_3,(C_{10}H_{17}\cdot NH_2,HCl)_2$, crystallises in needles; that of thallic chloride and atropine hydrochloride, $TlCl_3,C_{17}H_{23}O_3N,HCl$, in needles, and that with hyoscyamine hydrochloride, $TlCl_3,C_{17}H_{23}O_3N,HCl$, is a crystalline powder. β-Naphthylamine hydrochloride forms a crystalline *double* salt, $TlCl_3,(C_{10}H_7\cdot NH_2,HCl)_3$, whereas α-naphthylamine and aniline do not form salts but react with thallic chloride.

K. J. P. O.

Compounds of Thallic Chloride with Organic Bases. By Richard Jos. Meyer (*Ber.*, 1902, **35**, 1319. Compare Renz, preceding abstract).—A claim for priority. The difference between the results obtained by Renz and the author (compare Abstr., 1900, ii, 655) may be due to employment of different methods for the preparation of the thallic chloride compounds with the organic bases. G. T. M.

Condensation of Formaldehyde with 2-Picoline and 2-Ethylpyridine. By WILHELM KOENIGS and GUSTAV HAPPE (*Ber.*, 1902, **35**, 1343—1349).—2-Ethylpyridine is easily prepared by the reduction of 2-picolinealkine by means of zinc dust and hydriodic acid. It is shown that the compound obtained when 2-lutidylalkine is reduced in a similar manner is 2-*iso*propylpyridine (compare Abstr., 1891, 1119). In the preparation of 2-picolinealkine by the condensation of 2-picoline and formaldehyde, a small quantity of 2-*pyridylpropanediol*, $C_5NH_4\cdot CH(CH_2\cdot OH)_2$, is formed, and can be separated by means of the easily soluble *picrate*, which crystallises in slender needles and melts at 108—110°; the *platinichloride* crystallises in small needles which blacken and melt at 144—145°. 2-*Piperidylacetic acid*, obtained by the oxidation of 2-pipecolylalkine by chromic acid, crystallises from alcohol in small, slender needles melting at 214° and forms a crystalline *hydrochloride* melting at 180—182°, and a *platinichloride* which melts and decomposes at 203°. R. H. P.

p-Nitrophenyl-2-picolylalkine and its Derivatives. By R. KNICK (*Ber.*, 1902, **35**, 1162—1163).—*p-Nitrophenyl-2-picolylalkine* (2-*β-hydroxy-β*-p-*nitrophenylethylpyridine*), $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot C_5NH_4$, obtained by heating 2-picoline with *p*-nitrobenzaldehyde and water at 135—140° for 10 hours, crystallises from alcohol in lustrous, yellow leaflets and melts at 165°; the *platinichloride* crystallises in reddish leaflets which melt and decompose at 203°, the *aurichloride* is amorphous and melts at 105°, the *hydrochloride* crystallises in yellow leaflets melting at 215°, the *picrate* in small, yellow needles melting at 182°, and the *mercurichloride*, $C_{13}H_{12}O_3N_2\cdot HCl\cdot HgCl_2$, in long, yellow needles which decompose at 169°. The *benzoyl* derivative crystallises in white needles, melts at 192—193°, and forms an amorphous *platinichloride* which decomposes at 229°. 2-*β-Hydroxy-β*-p-*aminophenylethylpyridine*, obtained by reducing the nitro-compound with iron and hydrochloric acid, separates from alcohol in yellowish-red crystals which melt at 135° and turn red on exposure to air; the *hydrochloride* crystallises in small, yellow needles which decompose at 190°, the amorphous *platinichloride* decomposes at 195°, the *picrate* melts at 198° and decomposes at 202°, and the *mercurichloride* crystallises from water in brownish-yellow leaflets which sinter and begin to decompose at 171°. The *ketone*, $NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot C_5NH_4$, obtained when *p*-nitrophenyl-2-picolylalkine is oxidised by chromic acid, separates from alcohol or ether in yellow leaflets and melts at 160°; the *hydrochloride* crystallises in yellow leaflets melting at 218°, the *platinichloride* in red needles which melt at 181° and decompose at 187°, the *picrate* in yellow, silky needles melting at 175°, and the *mercurichloride* melts at 77°. The crystalline *oxime* melts at 152° and forms a *hydrochloride* which crystallises in yellow needles, blackens at 195°, and melts at 209°. The *phenylhydrazone* is an unstable substance which yields a *picrate* crystallising in dark yellow needles and melting at 155°. R. H. P.

Condensation of 4-Methyl-3-ethylpyridine with Formaldehyde. By WILHELM KOENIGS (*Ber.*, 1902, **35**, 1349—1557).—3-*Ethyl*-4-*pyridylpropanediol*, $C_5NH_3Et\cdot CH(CH_2\cdot OH)_2$, obtained when

4-methyl-3-ethylpyridine is heated with a 40 per cent. solution of formaldehyde in a sealed tube for 48 hours in a water-bath, separates from ethyl acetate in colourless crystals melting at 102—103° and forms a *hydrochloride* which crystallises in colourless, lustrous laminæ or needles melting at 122°, a *platinichloride* which separates from alcohol in small, compact crystals melting and decomposing at 170°, and a *picrate* which crystallises from ethyl acetate and melts at 115—116°. When oxidised with chromic acid, the diol yields 3-*ethylpyridine*-4-*carboxylic acid*, crystallises from alcohol in small, colourless needles, and melts at 216—217°.

4-Methyl-3-ethylpyridine does not condense with more than 2 mols. of formaldehyde. 3-*Ethylpyridyl*-4-*ethanol*, $C_5NH_3Et\cdot CH_2\cdot CH_2\cdot OH$, obtained when methylethylpyridine is heated with an alcoholic solution of formaldehyde for 36 hours, is an oil which forms a crystalline *picrate* melting at 110° and a *platinichloride* which crystallises in flat, yellow prisms melting and decomposing at 190—192°. The corresponding piperidine *compound*, obtained by reduction with sodium and alcohol, is a colourless oil and forms an *aurichloride* which crystallises in broad needles and melts at 122°. R. H. P.

Action of Benzyl Chloride and Iodide on Pyridine. II. By A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1901, **34**, 130—133. Compare Abstr., 1901, i, 484).—The action of benzyl haloid compounds on pyridine may give rise to hydrocarbons in the following two ways: (1) By the reduction of the haloid compound, yielding the corresponding saturated hydrocarbon; (2) by the removal of hydrogen chloride from the haloid compound, giving a hydrocarbon of the ethylene series; such hydrocarbons may also be formed from the elements of two mols. of the haloid derivative.

The interaction of benzyl chloride or iodide and pyridine, whether taking place in sealed tubes or open vessels, gives rise to toluene and to stilbene. T. H. P.

Action of Diphenylbromomethane on Pyridine. By A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 133—137).—1-*Bromo*-1-*diphenylmethylpyridine*, $CHPh_2\cdot C_5NH_5Br$, prepared by the action of diphenylbromomethane on pyridine, separates from aqueous alcohol in prismatic crystals containing $1H_2O$ and melting at 129—130°; it is readily soluble in water, alcohol, or acetone.

When treated with sodium picrate, the above compound yields 1-*diphenylmethylpyridone picrate*, $CHPh_2\cdot C_5NH_5\cdot O\cdot C_6H_2(NO_2)_3$, which separates from water, alcohol, or acetone in very slender needles melting and decomposing at 173—175°. The *platinichloride*,

$$(C_{18}H_{16}NCl)_2,PtCl_4,$$

is deposited from aqueous solution in golden scales melting at 195°.

When heated together in a sealed tube, diphenylbromomethane and pyridine give rise to diphenylmethane, tetraphenylethylene, and diphenylpyridylmethane, $CHPh_2\cdot C_5NH_4$; the last is probably a mixture of isomerides. T. H. P.

Action of Triphenylchloromethane and Triphenylbromomethane on Pyridine. By A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 137—140).—Triphenylbromomethane reacts energetically with dry pyridine, yielding bromodiphenylmethylpyridine (see preceding abstract), which under the action of the moisture of the air undergoes partial decomposition into triphenylcarbinol and pyridine hydrobromide.

The *compound*, $CPh_3\cdot OH,C_5NH_5$, obtained by the direct action of pyridine on triphenylcarbinol, is extremely soluble in benzene and is decomposed into its constituents on continuous heating at 80°.

Triphenylchloromethane has no apparent action on oxypyridine, but in the presence of moisture and excess of pyridine a reaction takes place similar to that obtained with the bromo-compound.

When heated with pyridine in sealed tubes, triphenylchloromethane or triphenylbromomethane yields triphenylmethane, together with an oily compound and basic products. T. H. P.

Preparation of Indoles from Pyrroles. By MAXIMILIAN DENNSTADT (D.R.-P. 125489. Compare Dennstadt and Voigtländer, Abstr., 1894, i, 259).—Indole is obtained by dissolving pyrrole in 10 per cent. sulphuric acid, allowing the product to remain for 1—2 hours, and then distilling the mixture with excess of sodium hydroxide in a current of steam.

Diethylindole, prepared from ethylpyrrole by a similar process, is a viscid oil with a disagreeable odour; it boils at 270—310° under the ordinary pressure. G. T. M.

Synthesis of 2- and 4-Hydroxyquinolines. By RUDOLF CAMPS (*Arch. Pharm.*, 1902, **240**, 135—146).—Phenacetyl-*o*-aminoacetophenone, $CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Ph$, on condensation yields a 2-hydroxyquinoline without any admixture of 4-isomeride (this vol., i, 178). This is evidently due to the negative character of the phenyl group; a similar result is obtained when this group is replaced by the groups CPhO, CMeO, CO_2Et, or CN, as will be seen below. It was not always possible to isolate the anilide, however; direct condensation to the quinoline often took place.

When *o*-aminoacetophenone is boiled for a little while, or heated for half-an-hour at 190—200° with ethyl benzoylacetate, 3-*benzoyl-2-hydroxy-4-methylquinoline* is at once formed. This melts at 264°; it has hardly any basic character; it forms a sodium salt, but it does not give any coloration with ferric chloride. If the two substances are heated only at 140—145° for half-an-hour, the main product is *benzoylacetyl-o-acetanilide*; this melts at 74—75° when crystallised from light petroleum; from benzene, it crystallises with some of the solvent and then melts at 65°. In alcoholic solution, it gives a violet coloration with ferric chloride, and so must be the enolic form, $CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot CH{:}CPh\cdot OH$. If the alcoholic solution is boiled, even for a few minutes only, it gives the ferric chloride reaction no longer; the crystals obtained from it then melt at 176°, losing water at the same time and forming the quinoline derivative; evidently these crystals are the ketonic form,

$$CH_3\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CPhO.$$

If the enolic form melting at 75° is suspended in alcohol and the solution allowed to remain for some time, reddish crystals are formed, less soluble in ether and melting at 104°; these also give the ferric chloride reaction, and presumably represent a second enolic form geometrically isomeric with the first.

Aminoacetophenone and ethyl acetoacetate yield only 3-*acetyl-2-hydroxy-4-methylquinoline*, which melts at 267°. Some anilide seemed to be formed, but it could not be isolated.

When aminoacetophenone and ethyl malonate are mixed and heated to boiling repeatedly, the main product is the *acetanilide* of 2-*hydroxy-4-methylquinoline-3-carboxylic acid*; this melts at 275° and is very stable towards alkalis, but is hydrolysed to the acid when it is heated for some time with fairly concentrated sulphuric acid. If the ketone and malonate are heated only at 170—175° for half-an-hour, there are formed in addition *ethyl acetylphenylmalonamate* (*ethyl malonate monoacetanilide*), $COMe\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot CO_2Et$, which is the main product, and symmetrical *diacetylphenylmalonamide* (*diacetanilide malonic acid*), $CH_2(CO\cdot NH\cdot C_6H_4\cdot COMe)_2$. The first of these is soluble in ether and melts at 55°; with sodium in ethereal solution, it yields a sodio-derivative. When boiled for some time with a solution of sodium hydroxide in dilute alcohol, it forms 2-*hydroxy-4-methylquinoline-3-carboxylic acid*, which melts at 254—255°, losing carbon dioxide and leaving 2-hydroxy-4-methylquinoline; if the boiling is continued only for a short time, the *ethyl ester* of this acid is obtained melting at 251—252°; this is also formed spontaneously from the sodio-derivative by loss of sodium hydroxide. The diacetylphenylmalonamide is insoluble in ether but soluble in benzene, unlike the anilide melting at 275°; it melts at 159—160°, losing water and forming the anilide just mentioned; boiling with dilute alcoholic sodium hydroxide also effects this conversion.

When aminoacetophenone and ethyl cyanoacetate are heated together at 200° for half-an-hour, 3-*cyano-2-hydroxy-4-methylquinoline* is formed; it melts at 320°, forms a sodium salt, and is stable to dilute acids and alkalis, but is hydrolysed to 2-hydroxy-4-methylquinoline-3-carboxylic acid when it is heated with strong sulphuric acid and a little water at 130—140°.

No success attended attempts to introduce halogens into the 3-position in the quinoline molecule by means of the corresponding acid chlorides. Aminoacetophenone and chloroacetyl chloride in ethereal solution give chloroacetylaminoacetophenone melting at 81°, but boiling with a slight excess of aqueous sodium hydroxide converts this into 2:3-dihydroxy-4-methylquinoline, the chloride being eliminated.

C. F. B.

8-Quinolinealdehyde. By Joh. Howitz (*Ber.*, 1902, **35**, 1273—1275).—8-*Iodomethylquinoline*, $C_9H_6N\cdot CH_2I$, prepared by the action of methyl iodide on the bromo-compound, crystallises from alcohol in colourless needles and melts at 84°.

8-*Quinolinealdehyde*, $C_9H_6N\cdot CHO$, prepared by oxidising the preceding compound with nitric acid (sp. gr. 1·3), crystallises from aqueous alcohol in long, white, glistening needles, melts at 94—95°, and is volatile with steam. The *platinichloride*, $2C_{10}H_7ON,H_2PtCl_6$, is a reddish-yellow, crystalline powder, can be recrystallised from hot alcoholic hydrochloric acid, and melts and decomposes at 250°. The aldehyde forms a bisulphite compound, an oxime, hydrazine, and anilino-derivative, reduces ammoniacal silver solutions, and on oxidation yields quinoline-8-carboxylic acid. T. M. L.

Products of Condensation of Tetramethyldiaminobenzhydrol with Primary Aromatic Amines, in which the Para-position is Occupied. By ALFRED GUYOT and M. GRANDERYE (*Compt. rend.*, 1902, **134**, 549—551).—With the object of preparing triphenylmethane derivatives, *p*-nitroaniline and tetramethyldiaminobenzhydrol were heated together at 100° in the presence of hydrochloric acid; *p*-nitrophenyl-leucauramine (Möhlau and Heinze, this vol., i, 243) is first formed, and on prolonged heating is converted into p-*dimethylaminobenzylidene*-p-*nitroaniline*, $NMe_2\cdot C_6H_4\cdot CH{:}N\cdot C_6H_4\cdot NO_2$; the latter crystallises in dichroic, orange plates melting at 198—199°; the *hydrochloride* forms violet needles melting at 193°.

With sulphanilic acid and the benzhydrol, no leucauramine is formed, the reaction leading to the direct formation of p-*dimethylaminobenzylidene*-p-*aminobenzenesulphonic acid*; *p*-phenylenediamine and the benzhydrol behave in a similar manner. K. J. P. O.

Sulphonic and Carboxylic Acids of the *as*-Dialkyl-*p*-phenylenediamines. KALLE & Co. (D.R.-P. 124907).—The sulphonic and carboxylic acids of the dialkyl-*p*-phenylenediamines are produced by heating 5-nitro-2-chlorobenzoic acid or 4-nitro-1-chlorobenzene-6-sulphonic acid with aqueous solutions of the aliphatic secondary amines, and subsequently reducing the resulting nitroamines.

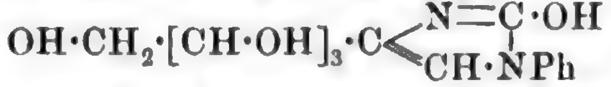
4-Nitrodimethylaniline-6-sulphonic acid, produced by heating together 4-nitro-1-chlorobenzene-6-sulphonic acid and dimethylamine in aqueous solution, yields 4-*aminodimethylaniline-6-sulphonic acid* when reduced with iron and acetic acid; this separates from water in lustrous crystals, develops an intense red coloration with ferric chloride, and gives rise to a blue colouring matter on oxidation with sodium thiosulphate in the presence of dimethylaniline.

4-Nitrodimethylaniline-6-carboxylic acid, prepared from 5-nitro-2-chlorobenzoic acid, crystallises in golden-yellow needles, and when reduced gives 4-*aminodimethylaniline-6-carboxylic acid*, a compound separating from alcohol in grey crystals melting at 178°.

G. T. M.

Dihydroxyketoethylenedinaphthylaminedisulphonic Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126443).—1 : 1′-*Dihydroxy*-6 : 6′-*ketoethylenedinaphthylamine*-3 : 3′-*disulphonic acid*, $OH\cdot C_{10}H_5(SO_3H)\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot C_{10}H_5(SO_3H)\cdot OH$, obtained by treating an alkaline solution of sodium 6-amino-α-naphthol-3-sulphonate with chloroacetyl chloride or the corresponding bromide, separates from the acidified product as a grey powder which readily dissolves in hot water; its sodium salt is very soluble, and is only partially precipitated on the addition of sodium chloride. The acid yields a yellow nitroso-compound on treatment with nitrous acid. G. T. M.

Method for the Detection of Glucosamine and its Employment on the Decomposition Products of Mucins. By H. Steudel (*Zeit. physiol. Chem.*, 1902, **34**, 353—384. Compare Abstr., 1901, i, 674).—The product obtained by the condensation of glucosamine with phenylcarbimide does not reduce Fehling's solution, and is probably *2-hydroxy-1-phenyl-4-αβγδ-tetrahydroxybutylglyoxaline*,



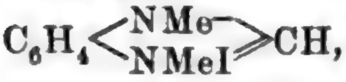
$$OH\cdot CH_2\cdot[CH\cdot OH]_3\cdot C{<}\begin{matrix}N{=}C\cdot OH\\ CH\cdot NPh\end{matrix}.$$

One part of the compound dissolved in 156·25 parts of water at the ordinary temperature and its solubility in alcohol is even less; it has $[\alpha]_D$ +76·9° at 20°.

Glucosamine and phenylcarbimide react in alkaline solution, yielding a sparingly soluble additive product. This has not been obtained in a pure state, but when boiled for some time with acetic acid it loses water and yields the above iminazole (glyoxaline) derivative. As the additive products of amino-acids with phenylcarbimide are only formed in acid solution, this affords a simple method for the separation of glucosamine and amino-acids.

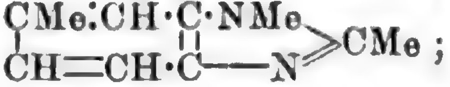
Glucosamine added to the products formed by the acid hydrolysis of proteids is readily precipitated by the phenylcarbimide method. The compounds with reducing properties obtained from submaxillary mucin and paramucin by hydrolysis with dilute acids contain no simple glucosamine and do not combine with phenylcarbimide. When, however, the reducing compound from paramucin is boiled with concentrated hydrochloric acid, glucosamine is formed and may be precipitated by the aid of phenylcarbimide. J. J. S.

Benziminazoles. By Otto Fischer and Moritz Rigaud (*Ber.*, 1902, **35**, 1258—1265. Compare this vol., i, 188).—The iodide,

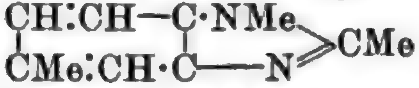


$C_6H_4{<}\begin{matrix}NMe-\\ NMeI\end{matrix}{>}CH$, obtained by methylating benziminazole is converted by freshly precipitated silver chloride into the analogous chloride, which crystallises from water in slightly yellow needles, with $1H_2O$, and melts when dry at 240°; the same salt is obtained from the carbinol base melting at 75° (Abstr., 1901, i, 413). On adding moist silver oxide to a solution of the methochloride, the ammonium base is formed, which is strongly alkaline and insoluble in ether; on boiling the solution, or on adding a little alkali, it is changed into the carbinol base which can be extracted with ether. Like ammonia, the ammonium base dissolves silver oxide, and on evaporating the solution silver is precipitated and N-dimethylphenylenecarbamide formed by the oxidation of the carbinol base.

4-Nitro-3-methylaminotoluene, $NO_2\cdot C_6H_3Me\cdot NHMe$, obtained by heating *p*-nitro-*m*-tolyl methyl ether (Reissert, Abstr., 1898, i, 315) with 33 per cent. aqueous methylamine for 4—5 hours at 160°, crystallises from dilute methyl alcohol in brownish-yellow prisms, melts at 83°, and yields, on reduction with tin and hydrochloric acid, a *base* which combines with boiling glacial acetic acid to form *1:2:6-trimethylbenziminazole*,

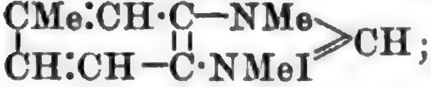
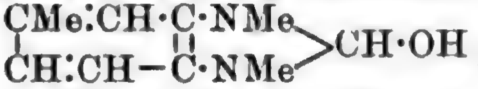
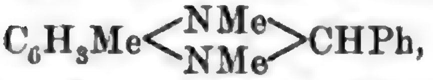


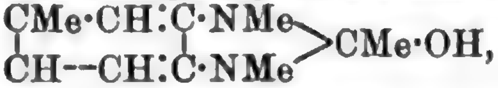
$\begin{matrix}CMe{:}CH\cdot C\cdot NMe\\ CH{=}CH\cdot C{-}{-}N\end{matrix}{>}CMe$; this crystallises from light petroleum in colourless prisms, melts at 122—123°, and yields a *platinichloride* (with $2H_2O$) decomposing at 259°, and an *aurichloride* melting at 189—190°; the *mercurichloride* forms long, white needles melting at 203—204°, and the *picrate* yellow prisms melting at 232—233°. The isomeric 1 : 2 : 5-trimethylbenziminazole,



$$\left.\begin{array}{l}\mathrm{CH{:}CH{-}C{\cdot}NMe}\\ \mathrm{CMe{:}CH{\cdot}C{-\!-}N}\end{array}\right>\mathrm{CMe}$$

(Abstr., 1893, i, 283), crystallises from water as a hydrate and then melts at 100°; when dry, it melts at 140°; the *picrate* forms yellow needles or stout prisms melting at 259—260°, and the *platinichloride* yellow plates (with $2H_2O$) melting at 251°; the *aurichloride* crystallises in needles and melts at 130—131°, and the *mercurichloride* melts at 199—200°.

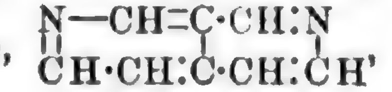
[With Ernst Becker.]—On heating 6-methylbenziminazole obtained from 3 : 4-tolylenediamine and formic acid for 4 to 5 hours at 140—150° with methyl alcohol (2 mols.) and methyl iodide (2 mols.), it yields almost quantitatively 1 : 6-*dimethylbenziminazole*-3-*methiodide*,  $\left.\begin{array}{l}\mathrm{CMe{:}CH{\cdot}C{-}NMe}\\ \mathrm{CH{:}CH{-}C{\cdot}NMeI}\end{array}\right>\mathrm{CH}$; this crystallises from dilute alcohol in long, transparent needles, melts at 227°, and is transformed by silver chloride into the analogous *methochloride* which melts at 275° and is identical with the chloride from the carbinol base (*infra*). On decomposing the chloride, or better, the iodide, with moist silver oxide, an alkaline solution of the ammonium base is given, which, on adding alkali, yields the *carbinol* base,  $\left.\begin{array}{l}\mathrm{CMe{:}CH{\cdot}C{\cdot}NMe}\\ \mathrm{CH{:}CH{-}C{\cdot}NMe}\end{array}\right>\mathrm{CH{\cdot}OH}$; this crystallises from benzene in stout needles, melts at 110°, and yields only salts of the ammonium type; the *aurichloride* melts at 160°, the *platinichloride* at 262°, and the *mercurichloride* at 220°. On oxidation with potassium permanganate, the carbinol yields N-dimethyltolylenecarbamide which melts at 106° (Pinnow and Sämann, Abstr., 1899, i, 943, give 103—104°). On hydrolysing either the foregoing carbinol base or the original methiodide with boiling aqueous sodium hydroxide, 3 : 4-*dimethylaminotoluene*, $C_6H_3Me(NHMe)_2$, is obtained as an oil which boils at 259—260° under 740 mm. pressure, and yields a *hydrochloride* crystallising in thick, colourless needles and melting at 125°. The diamine condenses with benzaldehyde yielding the *compound*  $C_6H_3Me\left<\begin{array}{l}\mathrm{NMe}\\ \mathrm{NMe}\end{array}\right>\mathrm{CHPh}$, which crystallises from dilute alcohol in long needles and melts at 88°; the analogous *derivative*, $C_{16}H_{18}ON_2$, of salicylaldehyde crystallises from dilute alcohol in yellow cubes and melts at 185°. When boiled with formic acid, the diamine yields the carbinol (m. p. 110°) from which it was obtained; with acetic acid, it yields 2-*hydroxy*-1 : 2 : 3 : 6-*tetramethyldihydrobenziminazole*,



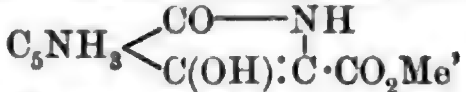
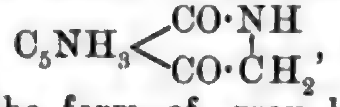
$$\left.\begin{array}{l}\mathrm{CMe{\cdot}CH{:}C{\cdot}NMe}\\ \mathrm{CH{-}{-}CH{:}C{\cdot}NMe}\end{array}\right>\mathrm{CMe{\cdot}OH},$$

which crystallises from light petroleum and melts at 148°.

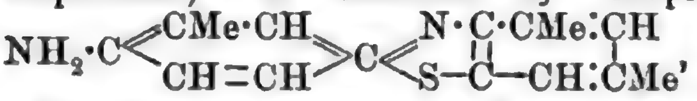
1-*Ethyl*-6-*methylbenziminazole*-3-*ethiodide*, obtained by heating the 6-methylbenziminazole with ethyl iodide and absolute alcohol for 10—12 hours at 150°, crystallises from alcohol in colourless needles and melts at 129°. The derived *carbinol* is a yellow oil which yields on hydrolysis 3 : 4-*diethylaminotoluene* as a thick oil giving a crystalline *hydrochloride*. W. A. D.

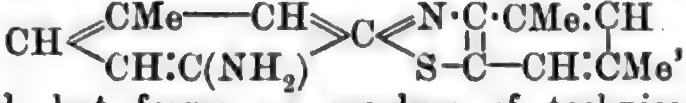
Derivatives of Cinchomeronic Acid. By Siegmund Gabriel and James Colman (*Ber.*, 1902, **35**, 1358—1367).—An attempt to prepare 2 : 7-benzodiazine,  $\begin{array}{l} N{-}CH{=}C{\cdot}CH{:}N \\ CH{\cdot}CH{:}C{\cdot}CH{:}CH \end{array}$, for which the name *copyrine* is proposed.

The *potassium* derivative of cinchomeronimide, which separates in lustrous, silvery laminæ when alcoholic potash is added to an alcoholic solution of the imide, reacts with ethyl chloroacetate, forming *ethyl cinchomeronylglycine*, $C_5NH_3{:}(CO)_2{:}N{\cdot}CH_2{\cdot}CO_2Et$, which crystallises in small, glistening needles and melts at 101°.

The glycine condenses with sodium methoxide, forming *methyl* 1 : 4-*dioxycopyrinecarboxylate*,  $C_5NH_3{<}\begin{array}{l} CO{-}NH \\ C(OH){:}C{\cdot}CO_2Me \end{array}$, which crystallises from a large quantity of water in bright yellow, flat, pointed needles melting and decomposing at 150°. When treated with hydrogen bromide or iodide in a reflux apparatus, it yields salts of 1 : 4-*dioxycopyrine*,  $C_5NH_3{<}\begin{array}{l} CO{\cdot}NH \\ CO{\cdot}CH_2 \end{array}$, from which the unstable base was obtained in the form of grey laminæ or pale yellow needles decomposing at about 195° ; the *hydrochloride*, *hydrobromide*, and *hydriodide* crystallise in orange-yellow laminæ, the *platinichloride* in orange-red needles decomposing at above 200°, and the *picrate* in orange-yellow needles or plates which sinter and decompose at 195°. When the base is treated with hydriodic acid under pressure, it is decomposed with the formation of 4-ethylpyridine-3-carboxylic acid, which crystallises from ethyl acetate in compact needles melting at 136—136·5° and forms an *aurichloride* crystallising in lustrous, golden laminæ and a *picrate* crystallising in long, lemon-coloured needles.

These derivatives of copyrine are all soluble in alkalis; such solutions, however, are readily oxidised by air or potassium persulphate yielding a red *base*, $C_{16}H_{10}O_4N_4$ (?), which forms a *hydrochloride* crystallising in orange-coloured, pointed needles. R. H. P.

Isomerides of the Base of the Dye "Erika." By Gustav Schultz and M. Tichomiroff (*J. pr. Chem.*, 1902, [ii], **65**, 150—160).—The dye "Erika" (sodium methylbenzenylaminothio-xylenolazo-α-naphtholdisulphonate) is obtained by coupling dehydrothio-*m*-xylidine,  $NH_2{\cdot}C{<}\begin{array}{l} CMe{\cdot}CH \\ CH{=}CH \end{array}{>}C{<}\begin{array}{l} N{\cdot}C{\cdot}CMe{:}CH \\ S{-}C{-}CH{:}CMe \end{array}$, with α-naphthol-ε-disulphonic acid. In the preparation of the base by heating *m*-xylidine with sulphur, the isomeric base iso*dehydrothio*-m-*xylidine*,



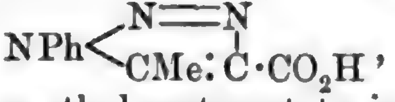
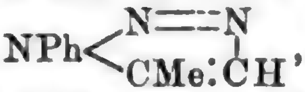
$$CH{<}\begin{array}{l} CMe{-}CH \\ CH{:}C(NH_2) \end{array}{>}C{<}\begin{array}{l} N{\cdot}C{\cdot}CMe{:}CH \\ S{-}C{-}CH{:}CMe \end{array},$$

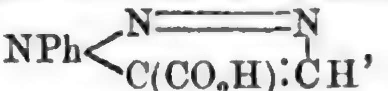
is also obtained, but forms no azo-dyes of technical value. Two attempts have been made to convert this second base into the Erika base. The first consisted of (i) diazotisation, by which a *diazochloride* melting and decomposing at 80—90° was obtained; (ii) replacement of the diazo-group by hydrogen, the resulting m-*methylbenzenyl*-p-*amino*-m-*thio-xylenol* being a substance which crystallises in yellow needles melting at 74·5; (iii) nitration of the thio-xylenol, by which two *mononitro*-derivatives melting at 152° and 146° respectively were obtained; (iv) reduction of the former (m. p. 152°), by which a *base* was obtained which crystallised in small, lustrous, red needles, and melted at 95°, but was not identical with the Erika base and did not yield any useful azo-dyes. The second attempt consisted of (i) nitration of the base by which a *mononitro*-derivative was obtained, which crystallised in yellow-red needles melting at 192°; (ii) diazotisation of the nitro-derivative (m. p. 192°); (iii) replacement of the diazo-group by hydrogen, by which the above-mentioned nitro-derivative (m. p. 146°) of the thio-xylenol was obtained, (iv) reduction of the nitro-derivative (m. p. 146°), by which a reddish *base* was obtained, which crystallises in slender, reddish needles melting at 89°, but was not identical with the Erika base. R. H. P.

Etherification of Carbinols by Alcohols. By OTTO FISCHER and KARL WEISS (*Chem. Centr.*, 1902, i, 471; from *Zeit. Farben. u. Textilchem.*, 1902, **1**, 1—3. Compare Abstr., 1901, i, 82).—*o*-Aminobenzyl alcohol and triphenylcarbinol cannot be induced to etherify with ethyl or benzyl alcohol either by prolonged boiling or by heating at 150°, whilst, on the other hand, the brilliant green base,

$$OH{\cdot}CPh(C_6H_4{\cdot}NEt_2)_2,$$

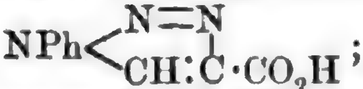
the crystal-violet base, $OH{\cdot}C(C_6H_4{\cdot}NMe_2)_3$, and tetramethyldiaminobenzhydrol, $OH{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, readily form ethers when boiled with these alcohols, and even react slowly with them in the cold. The ethers thus obtained resemble those of the malachite-green base in being colourless in the solid state or in solutions free from acids, but are hydrolysed and turned blue by the action of even weak acids such as carbonic or acetic acid. The violet base combines with phenol to form an additive *compound*, $OH{\cdot}C(C_6H_4{\cdot}NMe_2)_3,3PhOH$, which crystallises from a mixture of benzene and light petroleum in needles, melts at about 120°, and is readily soluble in alcohol or benzene, forming a blue solution, but only slightly so in ether or light petroleum. The *methyl ether* of the crystal-violet base, $C_{26}H_{33}ON_3$, separates from light petroleum in colourless crystals, melts at 158—159°, and is very readily soluble in benzene or ether, but less so in alcohol or light petroleum. The *ethyl ether*, $C_{27}H_{35}ON_3$, melts at 143—144°. The *benzyl ether*, $C_{32}H_{37}ON_3$, crystallises from light petroleum, melts at 174—175°, and is readily soluble in ether or benzene. The *methyl ether* of *tetramethyldiaminobenzhydrol*, $C_{18}H_{24}ON_2$, melts at 71—72° and is rather soluble in alcohol, ether, or benzene, but less so in light petroleum. The *ethyl ether* forms an oil which is easily soluble in ether, alcohol, or benzene, but less so in light petroleum; after remaining several months, this oil deposits crystals of the *anhydride* of *tetramethyldiaminobenzhydrol*, $C_{34}H_{42}ON_4$, which may be crystallised from a mixture of benzene and light petroleum, melts at 200—201°, and is hydrolysed by boiling with dilute acids regenerating the hydrol. The *benzyl ether* of *tetramethyldiaminobenzhydrol*, $C_{24}H_{28}ON_2$, crystallises in four-sided plates and melts at 102—103°. E. W. W.

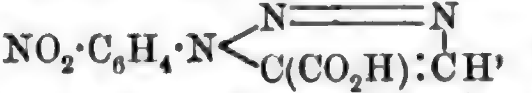
Synthesis of Derivatives of 1 : 2 : 3-Triazole. By OTTO DIMROTH (*Ber.*, 1902, **35**, 1029—1038).—1-*Phenyl-5-methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}N}\\ \mathrm{CMe{:}C{\cdot}CO_2H}\end{array}$, prepared by the action of phenylazoimide on ethyl acetoacetate in presence of sodium ethoxide, crystallises from water in prismatic needles and from benzene in scales and melts at 148° ; the *potassium* salt crystallises in flakes from dilute alcohol ; the *ammonium* salt separates from alcohol in a crystalline crust ; the *copper* salt forms blue prisms. The *methyl* ester, $C_{11}H_{11}O_2N_3$, crystallises from methyl alcohol in glistening flakes and melts at 73—74° ; the *ethyl* ester, $C_{12}H_{13}O_2N_3$, crystallises from a mixture of ether and light petroleum in flakes and melts at 60°. 1-*Phenyl-5-methyl*-1 : 2 : 3-*triazole*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}N}\\ \mathrm{CMe{:}CH}\end{array}$, prepared by heating the dry acid, crystallises from light petroleum in flakes, from dilute alcohol in prisms, melts at 64°, is not readily volatile with steam, exhibits basic properties, dissolves in hydrochloric acid, and forms a platinichloride. 1-*Phenyl*-1 : 2 : 3-*triazole-5-carboxylic acid*,



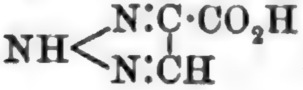
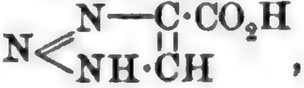
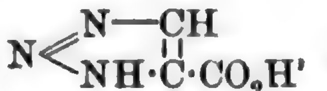
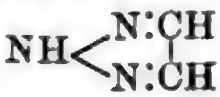
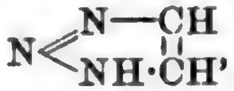
$$\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}N}\\ \mathrm{C(CO_2H){:}CH}\end{array},$$

prepared by oxidising the preceding compound with potassium permanganate, crystallises from alcohol in needles and melts at 176°, liberating carbon dioxide ; the *potassium* salt crystallises from alcohol in needles ; the *barium* salt, $C_{18}H_{12}O_4N_6Ba,2H_2O$, crystallises from water in needles ; the *copper* salt forms blue prisms and is insoluble in water ; the *methyl* ester, $C_{10}H_9O_2N_3$, crystallises from dilute methyl alcohol in minute needles and melts at 101° ; the *ethyl* ether crystallises from light petroleum in long needles and melts at 54—55° ; the *amide*, $C_9H_8ON_4$, crystallises from water in prisms and melts at 146° ; when heated, the acid is converted into 1-phenyl-1 : 2 : 3-triazole (Michael, Luehn, and Higbee, Abstr., 1898, i, 496).

1-Phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid (Zincke and Petermann, Abstr., 1901, i, 106) is formed on oxidising 1-phenyl-5-methyl-1 : 2 : 3-triazole-4-carboxylic acid. When cautiously heated alone, or when heated with water at 130—140°, it is converted into 1-*phenyl*-1 : 2 : 3-*triazole-4-carboxylic acid*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}N}\\ \mathrm{CH{:}C{\cdot}CO_2H}\end{array}$; this crystallises from methyl alcohol in prisms with 1MeOH, which is given off at 100°, and melts at 151° ; the *copper* salt forms small, blue prisms ; the *methyl* ester crystallises from methyl alcohol in prisms and melts at 121°. T. M. L.

Isomerism of the a-Triazole Compounds. By OTTO DIMROTH (*Ber.*, 1902, **35**, 1038—1047).—1-*Nitrophenyl*-1 : 2 : 3-*triazole-5-carboxylic acid*,  $\mathrm{NO_2{\cdot}C_6H_4{\cdot}N}<\begin{array}{l}\mathrm{N{=}N}\\ \mathrm{C(CO_2H){:}CH}\end{array}$, prepared by nitrating phenyltriazolecarboxylic acid, crystallises from spirit in minute, colourless needles and melts at 176°. 1-*Aminophenyl*-1 : 2 : 3-*triazole-5-carboxylic acid hydrochloride*, $C_9H_9O_2N_4Cl$, crystallises from hydrochloric acid in colourless, obliquely-truncated prisms ; it is oxidised by alkaline permanganate to an acid identical with Pechmann's *o*-triazolecarboxylic acid (Abstr., 1891, 1117), and this acid, when heated at 225°, gave Pechmann's *o*-triazole.

1-*Nitrophenyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid* crystallises from alcohol in prismatic needles. The *hydrochloride* of the *amino*-acid crystallises from dilute hydrochloric acid in colourless needles, melts at 200—202°, and is less soluble than the isomeride described above. Like the isomeride, it is oxidised to Pechmann's triazolecarboxylic acid, and the latter, when heated, is converted into Pechmann's crystalline triazole.

Contrary to the statement of Bladin (Abstr., 1894, i, 176), only one of the three carboxylic acids,  $NH<{N:C\cdot CO_2H \atop N:CH}$,  $N<{N—C\cdot CO_2H \atop NH\cdot CH}$, and  $N<{N—CH \atop NH\cdot C\cdot CO_2H}$, and only one of the triazoles,  $NH<{N:CH \atop N:CH}$ and  $N<{N—CH \atop NH\cdot CH}$, is capable of existing in a stable form. T. M. L.

Action of Hydrazobenzene and its Substitution Derivatives on Aldehydes.

By Berthold Rassow and Kurt Rülke (*J. pr. Chem.*, 1902, [ii], **65**, 97—122).—Benzaldehyde condenses with hydrazobenzene in the presence of acetic acid, forming dibenzylidenebenzidine. 2 : 4 : 6-Picrylphenylhydrazine, when warmed with an alcoholic solution of formaldehyde, yields 2 : 4-dinitro-6-nitrosoazobenzene. 4-Methylhydrazobenzene, when warmed with an alcoholic solution of formaldehyde, yields a *compound* which crystallises in white laminæ, melts at 190—193°, and is one of the two possible di-*p*-methyltetraphenylhexahydrotetrazines. *p*-Hydrazotoluene, in a similar manner, yields either (*a*) 1 : 2 : 4 : 5-*tetra*-p-*tolylhexahydro*-1 : 2 : 4 : 5-*tetrazine*,

$$CH_2:[N(C_6H_4Me)\cdot N(C_6H_4Me)]_2:CH_2,$$

which crystallises in yellowish, thin, monoclinic laminæ, melts at 213—214°, and is decomposed by mineral acids, or (*b*) *methylenedi*-p-*hydrazotoluene*, $CH_2[C_6H_4Me\cdot NH\cdot N(C_6H_4Me)]_2$, which crystallises from petroleum in small, monoclinic plates and melts at 156°. The analogous 1:2:4:5-*tetra*-p-*tolyl*-3:6-*dimethylhexahydro*-1:2:4:5-*tetrazine* was obtained from acetaldehyde and crystallises in yellowish, rhombic prisms, which melt at 150—151°. The corresponding *tetrazine* from *o*-hydrazotoluene and formaldehyde crystallises in small, colourless, rhombic needles, which melt and decompose at 187—188°, and the *tetrazine* from *m*-hydrazotoluene and formaldehyde in colourless rhombic needles which melt at 166·5—167·5°. R. H. P.

Reduction of Nitroaldehyde Hydrazones.

By Eugen Bamberger and Johannes Frei (*Ber.*, 1902, **35**, 1084—1093).—Ammonium sulphide readily reduces nitroaldehydrazones to arylhydrazoaldoximes of the type $NHAr\cdot NH\cdot CR:N\cdot OH$; it is probable that nitronic acids (this vol., i, 246), $Ar\cdot N:N\cdot CR:NO\cdot OH$, are first formed, and that these then undergo reduction to the oximes.

Phenylhydrazoformaldoxime, $NHPh\cdot NH\cdot CH:N\cdot OH$, obtained by passing dry hydrogen sulphide at a temperature not exceeding 40°, into an absolute alcoholic solution of α-nitroformaldehyde phenylhydrazone saturated with ammonia at 0°, crystallises from alcohol in white, lustrous needles and decomposes at 113·5°; it cannot be crystallised from hot solvents, and is converted by warm dilute mineral acids initially into formic acid, hydroxylamine, and phenylhydrazine, the last two interacting to form ammonia and a diazonium salt which ultimately yields phenol. Using α-nitroformaldehyde phenylhydrazone for the reduction, a considerable quantity of formazyl mercaptan is produced, but this is obviated and the yield of the hydrazoformaldoxime increased by employing the β-hydrazone. *Phenylazoformaldoxime*, $N_2Ph\cdot CH:N\cdot OH$, obtained by oxidising the hydrazo-compound with aqueous ferric chloride at 0°, crystallises from light petroleum in golden, felted needles, melts and decomposes at 94°, and is much more stable towards boiling water than the parent substance; it is, however, decomposed like the latter by warm dilute mineral acids.

Phenylhydrazoacetaldoxime, and *p*-chloro-, 2 : 4-dichloro-, and 2 : 4 : 6-trichloro-phenylhydrazoacetaldoxime (this vol., i, 247) were obtained in good yield by reducing the corresponding nitroacetaldoximes.

Phenylazobenzaldoxime, $N_2Ph\cdot CPh:N\cdot OH$, crystallises from a mixture of benzene and light petroleum in orange-yellow needles with a bronze-like lustre, and melts and decomposes at 134—135° (corr.).

Phenylhydrazopropionaldoxime, $NHPh\cdot NH\cdot CEt:N\cdot OH$, obtained from nitropropionaldehyde phenylhydrazone, crystallises from benzene on adding light petroleum in lustrous needles and melts at 87·5—88°; *phenylazopropionaldoxime* crystallises from light petroleum in radial aggregates of golden, silky needles and melts at 77·5—78°.

Phenylhydrazovaleraldoxime, prepared from nitrovaleraldehyde phenylhydrazone, forms white, silky needles melting and decomposing at 100·5—101°, and yields an *azo*-compound which crystallises from light petroleum or dilute alcohol in yellow, silky needles and melts at 103—103·5°. W. A. D.

Certain Properties of Azobenzene and Hydrazobenzene. By Paul Freundler and L. Béranger (*Compt. rend.*, 1902, **134**, 465—467).—Friedel and Crafts' reaction cannot be employed in preparing azo-ketones and azo-aldehydes by the action of acyl chlorides and aluminium chloride or bromide on azobenzene or diacetylhydrazobenzene, for these compounds simply form insoluble additive products with the aluminium salt but undergo no further change.

On acetylating a sample of hydrazobenzene containing azobenzene with acetic anhydride, a *compound* formed by the union of 2 mols. of diacetylhydrazobenzene and 1 mol. of azobenzene is obtained; this substance, $N_2Ph_2,2N_2Ph_2Ac_2$, crystallises from acetic acid, alcohol, carbon disulphide, or light petroleum in large, orange prisms and melts at 98·5—99°. This product is not decomposed into its generators by repeated crystallisation, but when heated at 190° under reduced pressure the azobenzene distils off, leaving the diacetylhydrazobenzene unchanged. The compound is also produced by warming an alcoholic solution of its generators, but no analogous combination takes place when mixtures of azobenzene with hydrazobenzene, its monoacetyl derivative, or acetanilide are employed. G. T. M.

Formazyl Phenyl Ketone. By EUGEN BAMBERGER and HUGO WITTER (*J. pr. Chem.*, 1902, [ii], **65**, 139—149).—Details of the preparation of compounds previously described (Abstr., 1893, i, 157; 1894, i, 98).
R. H. P.

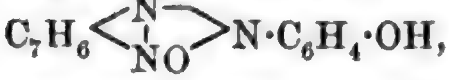
Action of Diazobenzene on Ethyl Acetoacetate, Acetoacetic Acid, and Ethyl Benzeneazoacetoacetate. By EUGEN BAMBERGER and E. W. WHEELWRIGHT (*J. pr. Chem.*, 1902, [ii], **65**, 123—138).—A detailed description of the preparation of compounds the formation of which has been previously described (Abstr., 1893, 84 and 156).
R. H. P.

Action of Sulphides, Sulphites, and Hydrosulphites on Nitrated Azo-colouring Matters. By AUGUSTE ROSENSTIEHL and E. SUAIS (*Compt. rend.*, 1902, **134**, 553—554. Compare Abstr., 1901, i, 429).—A nitrated azo-derivative is only attacked by an alkaline solution of calcium sulphide in such a way that the nitro-groups are converted into amino-groups, the calcium sulphide being oxidised to calcium thiosulphate. Sulphites, on the other hand, do not reduce the nitro-, but only the azo-group producing nitroanilines. *p*-Azoxyamines are attacked by sulphites, whilst the corresponding meta-derivatives are not touched. *p-Azoxy-o-toluidine*,

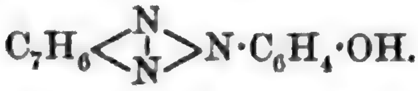
$ON_2(C_6H_3Me{\cdot}NH_2)_2$,

crystallises in brown needles melting at 188—189°. Hyposulphites easily reduce compounds which resist the action of sulphites; the nitrated azo-derivatives are converted into azoxyamino-derivatives; thus *m*-nitroazobenzene yields *m*-azoxyaniline (m. p. 150°).
K. J. P. O.

Reduction of *o*-Nitroazo-colouring Matters; Production of Derivatives of 2-Phenyl-ψ-aziminobenzene. By AUGUSTE ROSENSTIEHL and E. SUAIS (*Compt. rend.*, 1902, **134**, 606—608).—When the azo-colouring matters derived from *o*-nitroamines are treated in presence of an alkali with dextrose or an alkali sulphide, they yield quantitatively only one reduction product which is not affected by further treatment with the reducing agent. In this respect they differ markedly from the corresponding colouring matters derived from *m*- and *p*-nitroamines. The phenolazo-derivative from *o*-nitro-*p*-toluidine, $NO_2{\cdot}C_7H_6{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$, yields a colourless compound, $C_{13}H_{11}O_2N_3$, which melts at 240—241°, and forms a methyl derivative melting at 162—163°, and insoluble in alkali hydroxide solutions. When this product is treated with zinc and sodium hydroxide, it yields a crystalline compound which melts at 217—218°, and forms a methyl derivative melting at 102—103°. In this series of changes, the compound $NO_2{\cdot}C_7H_6{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$ is converted into the compound



$C_7H_6<\overset{N}{\underset{NO}{|}}>N{\cdot}C_6H_4{\cdot}OH$, and the latter into hydroxyphenyl-ψ-*o*-aziminotoluene,



$C_7H_6<\overset{N}{\underset{N}{|}}>N{\cdot}C_6H_4{\cdot}OH$.
C. H. B.

Action of Acylcyanoacetic Esters on Diazonium and Tetrazonium Chlorides. By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], **27**, 200—204).—The author has studied the action of benzene diazonium chloride and of diphenyltetra-azonium chloride on ethyl acetylcyanoacetate, ethyl propionylcyanoacetate, ethyl *iso*butyrylcyanoacetate, and ethyl benzoylcyanoacetate, and finds that, in general, diazonium and tetra-azonium chlorides act on the acylcyanoacetic esters with elimination of the acyl group and formation of the same substances as are produced by the action of diazonium and tetra-azonium chlorides on cyanoacetic esters. A. F.

Presence of Diazoamino- or Diazo-oxy-compounds in Azo-dyes. By WILHELM VAUBEL (*Chem. Centr.*, 1902, i, 464; from *Zeit. Farben.-Textilchem.*, 1902, 1, 3—4).—The presence of diazoamino- or diazo-oxy-compounds has been detected in the following dyes by boiling with concentrated hydrochloric acid:—Sodium aminoazo-xylenesulphonate and the dyes obtained from diazotised naphthionic acid and β-naphthol-γ-disulphonic acid, α-diazonaphthalene and β-naphthol-γ-disulphonic acid, diazotised naphthionic acid and naphthionate, diazonaphthalene-*o*-sulphonic acid and α-naphthol-4-sulphonic acid, and *p*-diazobenzenesulphonic acid and α-naphtholcarboxylic acid, all evolved nitrogen when thus treated. Nitrogen was not liberated in the following cases: aminoazobenzenesulphonic acid and the dyes prepared from diazotised naphthionic acid and α-naphthol, diazotised naphthionic acid and β-naphthol, β-diazoaphthalene and gallic acid, β-diazonaphthalene-1-sulphonic acid and Neville and Winther's acid, β-diazonaphthalene-1-sulphonic acid and β-naphthol, diazotised sulphanilic acid and β-naphthol, diazotised sulphanilic acid and β-naphtholmonosulphonic acid, and tetrazodiphenyl and naphthionic acid.

E. W. W.

Formation of Sugar from Proteids. By OSCAR LOEW (*Beitr. chem. Physiol. Path.*, 1902, 1, 567—575).—A theoretical consideration of the subject in reference to the structure of the proteid molecule.

W. D. H.

Production of Acetone from Crystallised Egg-albumin. By ARNOLD ORGLER (*Beitr. chem. Physiol. Path.*, 1902, 1, 583).—When crystallised egg-albumin is treated with hydrogen peroxide and copper sulphate, acetone is one of the products obtained. Blumenthal and Neuberg (Abstr., 1901, i, 433) show that the same is true for gelatin.

W. D. H.

Fission of Albumin by Papayotin. By OSKAR EMMERLING (*Ber.*, 1902, **35**, 695—699).—Blood fibrin, when dissolved in a dilute alkaline solution containing toluene, and treated with papayotin from *Carica papaya* (Merck's preparation), undergoes digestion and yields large quantities of albumoses and peptones, together with smaller amounts of arginine, tyrosine, leucine, aspartic acid, glycine, glutamic acid, alanine, and phenylalanine. The tyrosine separates from the original mother liquor; the albumoses, peptones, and arginine are precipitated by means of phosphotungstic acid, whilst the amino-acids remaining in the filtrate are converted into their ethyl esters by treatment with ethyl alcohol and hydrogen chloride, these esters being subsequently separated by fractional distillation under reduced pressure (10 mm.).

This result indicates that papayotin behaves in a similar manner to trypsin. G. T. M.

Fission of Albumin by Papayotin. By OSKAR EMMERLING (*Ber.*, 1902, **35**, 1012. Compare preceding abstract).—The hydrochloride of ethylglycine and not of ethyl glutamate is among the products formed. Phenylalanine is also probably present. J. J. S.

Physiological and Acid Proteolysis. By THOMAS BOKORNY (*Chem. Zeit.*, 1902, **26**, 113—114).—Acid proteolysis takes place in the cold, although the action is slow. Five hundred grams of minced beef were allowed to stand for 22 months with 500 c.c. of 5 per cent. sulphuric acid; on heating to the boiling point, the whole mass liquefied, showing that the fibre had been converted into acid albumin. Treatment with zinc sulphate solution proved that albumoses were present in large quantity and the phosphomolybdate test indicated the presence of peptones. Other experiments also prove that treatment in the cold with dilute acid causes peptonisation of meat.

Purified egg-albumin, when boiled for 2 hours with 4 per cent. solutions of acids, is attacked to the greatest extent by hydrochloric acid, then follow hydrobromic acid, sulphuric acid, and oxalic acid in that order; acetic acid is almost inactive. This treatment resembles the peptic digestion of albumin, whilst the treatment with concentrated acid resembles the tryptic digestion.

The action of moulds (*Penicillium* and *Aspergillus*) on egg-albumin has been investigated. The proteolytic action takes place best when the solution contains 0·25 to 1 per cent. of acid: the optimum temperature is 35° to 40°.

Blood-albumin is most easily digested by moulds; casein, egg-albumin, and legumin are only digested to the extent of about 1 per cent. when left for 40 hours at 35° with a 1 per cent. sulphuric acid solution to which a mould has been added. J. McC.

Abrin. By WALTHER HAUSMANN (*Beitr. chem. Physiol. Path.*, 1902, **2**, 134—142).—Abrin, which has been subjected to tryptic digestion and the proteids salted out, gives no biuret reaction; its poisonous characters remain unaltered, and it agglutinates red blood corpuscles as intensely as the unaltered abrin which contains proteids. Abrin, whether united to proteids or not, gives a precipitate with anti-abrin blood-serum. Abrin corresponds on the whole with ricin, but differs from it in that its agglutinating properties are resistant to pepsin—hydrochloric acid, even more resistant than its poisonous action. W. D. H.

Albumoid of Bone. By P. B. HAWK and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, *Amer. J. Physiol.*, **6**, xxvii—xxviii).—The collagenous residue, after extraction of the osseo-mucoid, when boiled in water yields an insoluble, elastin-like substance. It is more soluble in dilute acid and alkali than chondro-albumoid, and unlike the latter contains no loosely bound sulphur. It contains no phosphorus. Its percentage composition is, C, 50·03; H, 6·85; N, 15·93; S, 0·55; O, 26·64, which is very different from that of both elastin and keratin.
W. D. H.

Reactions of Various Mucoids. By L. D. MEAD and WILLIAM J. GIES (*Proc. Amer. Physiol. Soc.*, 1902, *Amer. J. Physiol.*, **6**, xxviii).—Further experiments which show that the various connective tissue mucoids are practically identical. W. D. H.

Soluble Compounds of Casein with Hydrogen Bromide or Iodide. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 124232).—*Casein hydrobromide*, a substance readily dissolving in warm water and containing 4 per cent. of bromine, is prepared by dissolving freshly precipitated casein in fuming hydrobromic acid; it is a white powder the solutions of which have a strongly acidic reaction. *Casein hydriodide* resembles the preceding compound, and is obtained in a similar manner. G. T. M.

The Coagulation of Casein by Rennet and by Lactoserum. By PAUL THEODOR MÜLLER (*Chem. Centr.*, 1902, i, 765—766; from *Münch. med. Woch.*, **49**, 372).—The power shown by the serum of animals which have been treated on Bordet's plan with milk proteids to precipitate caseinogen is dependent on the presence of calcium salts; barium salts will do instead, but magnesium and other salts are not effective. The specific serum, known as lactoserum, precipitates also boiled milk if a calcium salt is added. In the precipitation of caseinogen by means of lactoserum, no whey proteid is formed as in rennet coagulation. If the precipitate produced by lactoserum is dissolved by boiling with physiological salt solution, a precipitate is again produced by the addition either of lactoserum or rennet; in the latter case, whey proteid is also produced. The precipitability of the dissolved precipitate with ammonium sulphate is the same as that of fresh caseinogen; the conclusion is drawn that caseinogen is regenerated by boiling with physiological salt solution.

By strong acetic acid, a precipitate of the "precipitin" in an active condition is obtained from lactoserum. Lacto-precipitin is rendered inactive by prolonged heating at 70°, and acquires the property of inhibiting the precipitating action of fresh lactoserum. If the precipitin of lactoserum is removed by the addition of caseinogen, the residue has no such inhibiting characters; in this connection, calcium salts have no action. The inhibiting substance is precipitated by dilute acetic acid. After some hours, inactive lactoserum is able to dissolve the caseinogen precipitated by lactoserum; this property is not possessed by normal inactive rabbit's serum. Lactoserum, deprived of its precipitin by the addition of milk, acquires no inhibiting properties on subsequent heating to 75°; the inhibiting substance thus appears to be derived from the precipitin by the action of heat. Whilst normal inactive rabbit's serum has no anti-rennet action, inactive lactoserum inhibits the action of both rennet and fresh lactoserum. In the case of rennet curdling, excess of caseinogen neutralises the inhibiting effect. The inhibiting action is explained by the capacity of the inhibiting material to unite with caseinogen, and so shield it from the action of coagulating agents. The inhibiting substance, being a derivative of precipitin, is regarded as analogous to Eisenberg and Volk's "agglutinoids" and precipitoids, and in the light of Ehrlich s theory this is compared to "receptors," the zymophore group of which is destroyed by heat, leaving the haptophore group untouched. W. D. H.

Elastin, Mucoid, and other Substances in Elastic Tissue. By A. N. Richards and William J. Gies (*Amer. J. Physiol.*, 1902, **7**, 93—134).—Elastin has the following average percentage compositions: C, 54·14; H, 7·33; N, 16·87; S, 0·14; O, 21·52. No sulphur can be split off as sulphide by boiling with alkali. On decomposition with acid, only small proportions of nitrogen can be split off as ammonia and hexon bases, of which arginine, lysine, and histidine were identified. Elastin is not a 'fat proteid compound.' It digests readily in pepsin-hydrochloric acid; of the products, proto-elastose is most abundant, and the small amount of peptone points to resistance in the elastoses to progressive zymolysis. The combustion equivalent of elastin is 5925 calories. Elastic ligament contains mucoid having the general properties of the other gluco-proteids of connective tissues. The proteids present coagulate at 50°, 65°, 75°, and 82°; these do not appear to arise wholly from adherent blood and lymph. There is also a small amount of nucleo-proteid; the composition of the gelatin obtained indicates that the collagen of elastic tissue is identical with that of bone and tendon. The combustion equivalent of the gelatin is 5276 cal. Among the crystalline extractives obtained from *ligamentum nuchæ* were creatine, hypoxanthine, and guanine. W. D. H.

Influence of Carbon Dioxide on the Action of Diastase. By Otto Mohr (*Ber.* 1902, **35**, 1024—1029).—Maltose is not formed to any large extent by the action of diastase on starch when alkaline or neutral, although it is produced from acid samples of starch. In presence of carbon dioxide, however, about 30 per cent. of the starch is converted into maltose, whatever the nature of the sample of starch employed.

In presence of 0·01 gram of asparagine per 2·5 grams of starch, carbon dioxide further assists the formation of maltose, but hinders it if more than 0·05 gram of asparagine is present. Similarly, traces of lactic acid facilitate sugar-formation, but the action is less powerful if the quantity of acid is increased, or if carbon dioxide is also present.

T. M. L.

A New Method of Observing Peptic Activity. By E. I. Spriggs (*J. Physiol.*, 1902, **28**; *Proc. Physiol. Soc.*, v—vi).—The viscosity of proteid solution in the presence of pepsin and 0·4 per cent. hydrochloric acid was estimated by an Ostwald's viscometer, and was found to fall rapidly. A fall also occurs, but more slowly, when the acid without the pepsin is present. As the viscosity falls the amount of coagulable proteid diminishes. Expressed in the form of a curve, the fall is first rapid, then slower, and finally insignificant; by this time, the coagulable proteid has nearly disappeared. A definite viscosity was found to correspond with a constant proportion between coagulable and non-coagulable proteid. The curves are capable of mathematical treatment, and there are indications that a simple ratio exists between the amount of pepsin and the time required to produce a given amount of chemical change. W. D. H.

Pepsin. By Cornelis A. Pekelharing (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 412—423; *Zeit. physiol. Chem.*, 1902, **35**, 8—30).—Slow precipitation of pepsin by ammonium sulphate causes it to separate out in the form of globulites; it was, however, not possible to obtain in this way a substance of constant composition. Better results may be obtained by dialysing dog's gastric juice (procured by Pawloff's method); when the percentage of hydrochloric acid sinks to 0·02 per cent., the pepsin is precipitated in the form of globulites. Six specimens of pepsin were prepared and analysed, and found to have a constant percentage composition. It is thus shown to be a proteid, and is free from phosphorus if care is taken to filter the gastric juice from its mucoid, nucleo-proteid; it, however, contains chlorine. Peptic activity is proportional to the amount of this proteid present, and is lost at the temperature at which the proteid is coagulated. It also exerts a rennet action on milk, causes the formation of plastein from albumose, but, unlike the original gastric juice, has no action on fats. On decomposition, it yields xanthine and a pentose; a proteid-like organic acid (*pepsinic acid*) is also described, having the composition C, 50·79; H, 7·02; N, 14·44; S, 1·08. W. D. H.

Artificial Pepsin Digestions in the Presence of Alcohol. By Eug. Thibault (*J. Pharm. Chim.*, 1902, [vi], **15**, 5—13).—Alcohol and glycerol have a decided retarding influence on the digestive action of pepsin. In the case of the former, the lowest dilution at which any appreciable retarding influence is noticed is when the liquid contains about 4 per cent. of alcohol (90°), and in the latter, when the liquid contains 20 per cent. of glycerol. H. R. Le S.

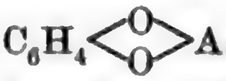
Chemical Nature of Tetanus Toxin. By H. Hayashi (*Chem. Centr.*, 1902, i, 272; from *Arch. exp. Path. Pharm.*, 1901, **47**, 9—18).—The properties of the tetanus poison point to its being a proteid, probably a primary proteose. W. D. H.

Aromatic Arsenic Compounds. By August Michaelis (*Annalen*, 1902, **320**, 271—344. Compare Abstr., 1883, 183, 327; 1885, 526; 1887, 367; 1892, 1321; 1894, i, 187).—Phenylchloroarsine, $AsPhCl_2$, when treated in ethereal solution with the sodium derivatives of alcohols and phenols, yields the corresponding esters of the hypothetical phenylarsenious acid, $AsPh(OH)_2$.

[With P. Fromm.]—*Dimethyl phenylarsenite*, $AsPh(OMe)_2$, a colourless liquid with characteristic odour, boils at 116° under 18 mm. and at 220° under the ordinary pressure; it has a sp. gr. 1·343 at 20°. The ester is at once decomposed by water or alkaline solutions, yielding phenylarsenious oxide, AsPhO, and methyl alcohol; it forms a chlorine *additive* compound, $AsPh(OMe)_2Cl_2$, which, on treatment with water, gives rise to phenylarsenic acid, $AsPhO(OH)_2$, methyl alcohol, and hydrochloric acid.

Diethyl phenylarsenite, $AsPh(OEt)_2$, boils at 122° under 15 mm. pressure and yields a chlorine *additive* compound, $AsPh(OEt)_2Cl_2$.

Diphenyl phenylarsenite, $AsPh(OPh)_2$, is an oily liquid boiling at 245° under 15 mm. pressure; it has a sp. gr. 1·32 at 20°; under the action of chlorine, it gives rise to phenylarsenic tetrachloride, $AsPhCl_4$, and trichlorophenol. The corresponding p-*tolyl* ester boils at 285° under 12 mm. pressure and has a sp. gr. 1·2989 at 13°; the *benzyl* ester is an oil having the odour of benzyl alcohol and boiling at 296° under 30 mm. pressure; it has a sp. gr. 1·2853 at 13°. *Di-β-naphthyl phenylarsenite*, $AsPh(O\cdot C_{10}H_7)_2$, crystallises in colourless needles melting at 113—114°; it resembles the preceding esters in being readily decomposed by water with the formation of phenylarsenious oxide.

Catechol phenylarsenite,  $C_6H_4\!<\!{}^{O}_{O}\!>\!AsPh$, prepared by treating the lead derivative of catechol with a xylene solution of phenylchloroarsine, is a white, crystalline substance melting at 83° and boiling at 197—198° under 15 mm. pressure. The interaction of phenylchloroarsine and the sodium derivative of catechol results in the formation of a substance still containing chlorine.

Phenylarsenimide, $AsPh\colon NH$, produced by passing dry ammonia gas into a benzene solution of phenylchloroarsine, is a crystalline substance readily decomposed by moisture into phenylarsenious oxide and ammonia; it crystallises from alcohol in leaflets, sinters at 265°, and melts at 270°.

The esters of phenylarsenic acid are most readily obtained by the action of the alkyl iodides on *silver phenylarsenate*, $AsPhO(OAg)_2$; this salt, which is prepared from silver nitrate and a solution of neutral ammonium phenylarsenate, crystallises in nacreous plates.

Dimethyl phenylarsenate, $AsPhO(OMe)_2$, is a colourless liquid with a disagreeable odour boiling at 188° under 95 mm. pressure; it has a sp. gr. 1·3946 at 23°. The corresponding *ethyl* ester boils at 168—170° under 15 mm. pressure and has a sp. gr. 1·318 at 15°; chlorine converts it into phenyloxychloroarsine, chloral, and hydrogen chloride. Both esters are decomposed by water yielding phenylarsenic acid and the corresponding alcohol.

[With V. BRUDER.]—Dimethylaminophenylarsenic acid,

$$NMe_2\cdot C_6H_4\cdot AsO(OH)_2,$$

prepared by treating dimethylaminophenylarsenious oxide with water and red mercuric oxide, crystallises in long, colourless needles which sublime without melting.

[With K. ULRICH.]—Phenyldiethylarsine, $AsPhEt_2$, combines with methyl iodide at the ordinary temperature to form *phenylmethyldiethylarsonium iodide*, $AsPhEt_2MeI$, which crystallises in prisms melting at 122°.

Phenyltriethylarsonium iodochloride, $AsPhEt_3\cdot ICl_2$, produced by passing chlorine into an acetic acid solution of the quaternary iodide, separates in dark yellow crystals.

Phenyliodomethyldiethylarsonium iodide, $AsEt_2PhI\cdot CH_2I$, produced by heating phenyldiethylarsine with methylene iodide on the water-bath, crystallises from dilute alcohol in needles and melts at 173°.

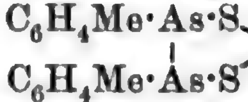
Phenyldiethylarsenobetaine chloride, $AsPhEt_2Cl\cdot CH_2\cdot CO_2H$, obtained by warming a mixture of phenyldiethylarsine and chloroacetic acid, crystallises from ether and alcohol in white needles and melts at 135°; it is readily soluble in water. The *platinichloride* forms lustrous, red crystals melting at 161°. The betaine is set free by the action of alcoholic potassium hydroxide; the corresponding *ethyl* ester, $AsPhEt_2Cl\cdot CH_2\cdot CO_2Et$, obtained by heating the arsine with ethyl chloroacetate at 100°, crystallises in needles and melts at 125°; its crystalline picrate melts at 90°.

When pure, anisylchloroarsine melts at 48° and boils at 160° under 30 mm. pressure. Anisylarsenic acid (m. p. 203°), when heated with phosphorus acid, yields *arsenoanisole*, $OMe\cdot C_6H_4\cdot As\colon As\cdot C_6H_4\cdot OMe$, this substance being a yellow, amorphous powder decomposing at 200°.

[With H. Hilbenz.]—*Phenetylchloroarsine*, $OEt\cdot C_6H_4\cdot AsCl_2$, produced by heating triphenetylarsine with arsenious chloride at 220°, is a colourless liquid boiling at 198° under 28 mm. pressure; dry chlorine converts it into a solid *tetrachloride*, *phenetylarsenic acid*, $OEt\cdot C_6H_4\cdot AsO(OH)_2$ (m. p. 209—210°), being formed in the presence of water; sodium carbonate yields the *oxide*, $OEt\cdot C_6H_4\cdot AsO$. *Arsenophenetole*, $OEt\cdot C_6H_4\cdot As\colon As\cdot C_6H_4\cdot OEt$, is a yellow powder which readily becomes resinous.

[With K. Ulrich and F. Ziegler.]—*p*-Tolylchloroarsine crystallises in colourless, refractive plates melting at 31° and boiling at 267° under the ordinary pressure. *Arseno*-p-*toluene*, $C_6H_4Me\cdot As\colon As\cdot C_6H_4Me$, obtained by the action of phosphorous acid on *p*-tolylarsenious oxide, crystallises from chloroform in lustrous needles and melts at 184°; chlorine converts it successively into di- and tetra-chlorides, nitric acid oxidises it to *p*-tolylarsenic acid.

p-*Tolylarsenious sulphide*, $C_6H_4Me\cdot AsS$, produced by passing hydrogen sulphide into an alcoholic solution of the corresponding oxide, separates from benzene in white, lustrous crystals and melts at 146°.

p-*Tolylarsenic sesquisulphide*,  $\left.\begin{matrix}C_6H_4Me\cdot As\cdot S\\ \vert\\ C_6H_4Me\cdot As\cdot S\end{matrix}\right>S$, resulting from the action of hydrochloric acid on an ammoniacal solution of *p*-tolylarsenic acid saturated with hydrogen sulphide, is separated from the sulphur simultaneously set free by solution in benzene; it crystallises from this solvent in white needles and melts at 119—120°.

[With H. Klatt.]—p-*Tolyldimethylarsine*, $C_6H_4Me\cdot AsMe_2$, prepared by treating the chloroarsine with excess of zinc methyl in ethereal solution, is a colourless liquid having a disagreeable odour and boiling undecomposed at 220° in an atmosphere of carbon dioxide; the *quaternary iodide*, $C_6H_4Me\cdot AsMe_3I$, crystallises from water in plates which dissociate on heating; the *platinichloride*, $(C_6H_4Me\cdot AsMe_3)_2PtCl_6$, forms reddish-yellow leaflets and melts at 225°. *Tolyl*-p-*diethylarsine* is a colourless, refractive liquid boiling at 250°; its *methiodide*, $C_6H_4Me\cdot NEt_2,MeI$, crystallises in colourless leaflets and melts at 220°; the *ethiodide* is crystalline, has a bitter taste, and melts at 230°; the *platinichloride* forms reddish-yellow leaflets melting at 210°.

[With Eppenstein.]—p-*Oxydiethylarsinibenzoic acid* is obtained in the form of its *hydrochloride*, $CO_2H\cdot C_6H_4\cdot AsEt_2O,HCl$ or

$$CO_2H\cdot C_6H_4\cdot AsEtCl\cdot OH,$$

by oxidising diethyl-*p*-tolylarsine with an aqueous solution of potassium permanganate, saturating the filtrate with hydrogen chloride, evaporating to dryness, and crystallising the residue from alcohol; the salt forms white crystals melting at 162°, and yields the *mercurichloride*, $CO_2H{\cdot}C_6H_4{\cdot}AsEt_2O,HCl,HgCl_2$, a white substance melting at 182°.

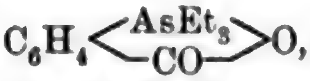
p-*Thiodiethylarsinibenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}AsEt_2S$, produced by the action of hydrogen sulphide on an aqueous solution of the preceding compound, crystallises from water in long, colourless needles and melts at 184°.

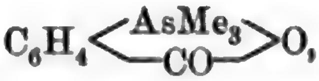
p-*Diethylarsinobenzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}AsEt_2$, obtained by reducing the preceding oxy-acid with tin and hydrochloric acid, crystallises in white needles and melts at 58°; it forms additive compounds with sulphur and methyl iodide, its *metallic* salts, excepting those of the alkali metals, are insoluble; its *mercurichloride*, $CO_2H{\cdot}C_6H_4{\cdot}AsEt_2,HgCl_2$, crystallises in white, silky leaflets and melts at 171—172°.

The halogens form additive products with this acid, which readily absorb moisture, giving rise to the corresponding halogen salt of *p*-oxydiethylarsinibenzoic acid; the *hydrobromide*,

$$CO_2H{\cdot}C_6H_4{\cdot}AsEt_2O,HBr,$$

melts at 144—145°, and the hydriodide at 84°. The *methiodide* of *p*-diethylarsinobenzoic acid, $CO_2H{\cdot}C_6H_4{\cdot}AsEt_2,MeI$, forms white needles melting at 131°.

p-*Triethylarsenibenzobetaine*,  $C_6H_4\left<\begin{matrix}AsEt_3\\CO\end{matrix}\right>O$, prepared by oxidising *p*-tolyltriethylarsonium chloride with alkaline permanganate solution, forms a hygroscopic *hydrochloride* from which it is obtained by alkalis; it crystallises in hygroscopic plates having a bitter taste and does not form salts with alkali hydroxides; it is completely decomposed by alcoholic potassium hydroxide, yielding triethylarsenious oxide and potassium benzoate. The *platinichloride*, $(CO_2H{\cdot}C_6H_4{\cdot}AsEt_3)_2PtCl_6$, forms pale yellow leaflets melting at 225°; the *aurichloride* crystallises in golden-yellow needles and melts at 165°; the *picrate* separates in yellow leaflets melting at 155°.

p-*Trimethylarsenibenzobetaine*,  $C_6H_4\left<\begin{matrix}AsMe_3\\CO\end{matrix}\right>O$, crystallises in leaflets, with $2\frac{1}{2}H_2O$; the *hydrochloride* and *hydrobromide* separate from water in white needles decomposing respectively at 400° and 270°; the *platinichloride* and *aurichloride* form yellow needles melting respectively at 255° and 198°; the *nitrate* is obtained in leaflets melting at 230°.

Nitro-p-*tolylarsenic acid*, $NO_2{\cdot}C_6H_3Me{\cdot}AsO(OH)_2$, prepared from *p*-tolylarsenic acid by the action of nitrosulphuric acid, crystallises in rhombic prisms and does not melt below 300°; the alkali and *silver* salts are amorphous; the *acid barium* salt, $[NO_2{\cdot}C_6H_3Me{\cdot}As(OH){\cdot}O]_2Ba$, separates from its aqueous solution in white needles; the *calcium* salt forms lustrous leaflets. The salts retain $1H_2O$ very tenaciously even at 180°. *Amino*-p-*tolylthioarsenic acid*, $NH_2{\cdot}C_6H_3Me{\cdot}AsS(SH)_2$, obtained by reducing the preceding acid with ammonium sulphide, is isolated in the form of its *sulphate*, a yellow, amorphous powder decomposing at 155°. *Nitro*-p-*carboxyphenylarsenic acid*,

$$NO_2{\cdot}C_6H_3(CO_2H){\cdot}AsO(OH)_2,$$

produced by oxidising nitro-*p*-tolylarsenic acid with alkaline permanganate, crystallises in white needles soluble in water or alcohol; it does not melt below 300°.

Dinitroarseno-p-*toluene*, $As_2(C_6H_3Me{\cdot}NO_2)_2$, formed by the action of phosphorous acid on nitro-*p*-tolylarsenic acid, is a yellow substance melting at 165°; when treated with bromine, it yields *nitro*-p-*tolylbromoarsine*, $NO_2{\cdot}C_6H_3Me{\cdot}AsBr_2$, which separates from chloroform in light brown, lustrous scales decomposing at 260°.

Nitro-p-*tolylarsenious sulphide*, $NO_2{\cdot}C_5H_3Me{\cdot}AsS$, produced on passing hydrogen sulphide into an aqueous solution of nitro-*p*-tolylarsenic acid, is separated from the sulphur deposited by dissolving in ammonia solution or in benzene; it is obtained in yellow needles melting at 141—142°.

o-*Dimethylamino*-p-*tolylarsenious oxide*, $NMe_2{\cdot}C_6H_3Me{\cdot}AsO$, prepared by heating a mixture of arsenious chloride and dimethyl-*o*-toluidine, is a white, amorphous powder melting at 55°.

o-*Dimethylamino*-p-*tolylchloroarsine hydrochloride*,

$$AsCl_2{\cdot}C_6H_3Me{\cdot}NMe_2,HCl,$$

resulting from the action of concentrated hydrochloric acid on the preceding oxide, crystallises in needles having a pungent odour and melting at 145°; the *hydrobromide* is obtained in rhombic plates melting at 168°; the *hydriodide* is a red, crystalline powder; the *sulphide*, $S{\cdot}NMe_2{\cdot}C_6H_3Me{\cdot}AsS$, formed by passing hydrogen sulphide into an alcoholic solution of the oxide, separates as a pale yellow powder and melts at 65—67°. oo-*Tetramethyldiaminoarseno*-p-*toluene*,

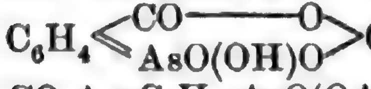
$$As_2(C_6H_3Me{\cdot}NMe_2)_2,$$

prepared from the oxide and phosphorous acid in alcoholic solution, is a pale yellow powder melting at 75°.

o-*Dimethylamino*-p-*tolylarsenic acid*, $NMe_2{\cdot}C_6H_3Me{\cdot}AsO(OH)_2$, obtained from the oxide by the action of water and red mercuric oxide, forms grey leaflets and melts at 245°.

[With HERMANN EISENLOHR.]—m-*Tolylchloroarsine* is a refractive oil boiling at 270°; the *tetrachloride*, $C_6H_4Me{\cdot}AsCl_4$, melts at 38°; the *oxide*, $C_6H_4Me{\cdot}AsO$, obtained by treating the chloroarsine with sodium carbonate, is a fibrous, viscid mass, which yields m-*arsenotoluene*, (m. p. 106°) on treatment with phosphorous acid.

m-*Tolylarsenic acid*, produced from the tetrachloride, crystallises in needles and melts at 150°; when heated at 220—230°, it yields the *anhydride*, $C_6H_4Me{\cdot}AsO_2$; its *ammonium hydrogen*, *phenylhydrazine hydrogen*, *calcium*, and other *metallic* salts are described.

m-*Carboxyphenylarsenic acid*, $CO_2H{\cdot}C_6H_4{\cdot}AsO(OH)_2$, obtained by oxidising the preceding acid, crystallises in lustrous leaflets and yields the anhydride, $CO_2H{\cdot}C_6H_4{\cdot}AsO_2$, on heating; its *calcium* salt,  $C_6H_4<\begin{array}{l}CO\text{———}O\\ AsO(OH)O\end{array}>Ca$, crystallises in four-sided-plates; the *silver* salt, $CO_2Ag{\cdot}C_6H_4{\cdot}AsO(OAg)_2$, is a white precipitate.

[With R. SEEMANN.]—m-*Xylylchloroarsine* crystallises in colourless needles melting at 42—43°; the *tetrachloride*, $C_8H_9AsCl_4$, is a white, crystalline mass yielding the *oxychloride*, $C_6H_3Me_2{\cdot}AsOCl_2$ (m. p. 150°), and the *acid*, $C_6H_3Me_2{\cdot}AsO(OH)_2$, on treatment with water. m-*Xylyl*-

arsenious oxide, $C_6H_3Me_2{\cdot}AsO$, melts at 220°, and the *sulphide*, $C_6H_3Me_2{\cdot}AsS$, crystallises in white needles melting at 169°. *Arseno*-m-*xylene* crystallises from chloroform in lustrous, white needles and melts at 194—196°; the additive product, *iodoarseno*-m-*xylene*, $C_6H_3Me_2{\cdot}AsI{\cdot}AsI{\cdot}C_6H_3Me_2$, melts at 89°. *m*-Xylylarsenic acid is also obtained by oxidising the chloroarsine or the corresponding oxide; it forms quadratic crystals and melts at 210°; its *ammonium* salt melts at 136°. *Monochloro*-m-*xylylarsenic acid*, $C_6H_2Me_2Cl{\cdot}AsO(OH)_2$, results from the oxidation of the chloroarsine or the preceding compound with chlorine in aqueous solution; it crystallises in needles and melts at 165°; *dichloro*-m-*xylylarsenic acid*, $C_6HMe_2Cl_2{\cdot}AsO(OH)_2$, formed by oxidation with chlorine in glacial acetic acid, melts at 193°. *Nitro*-m-*xylylarsenic acid* crystallises in white needles melting at 207°. m-*Carboxytolylarsenic acid*, $CO_2H{\cdot}C_6H_3Me{\cdot}AsO(OH)_2$, obtained from the xylyl acid with permanganate solution, does not melt below 300°; *dicarboxyphenylarsenic acid*, $C_6H_3(CO_2H)_2{\cdot}AsO(OH)_2$, is produced when a double quantity of oxidising agent is employed.

[With PASEL.]—p-*Xylylchloroarsine* is obtained in needles melting at 285°; the *oxide* melts at 165° and yields the *iodoarsine*, $C_8H_9AsI_2$ (m. p. 45°), with concentrated hydriodic acid and the *oxychloroarsine* with chlorine, the latter derivative melting at 178°. *Arseno*-p-*xylene* melts at 208° and its *di-iodide* at 97°. p-*Xylylarsenious sulphide* C_8H_9AsS, melts at 188° and the *disulphide* at 95°. p-*Xylylarsenic acid* crystallises in needles melting at 223°; its *nitro*-derivative forms pale yellow needles, melts at 205°, and when treated with phosphorous acid yields *arsenonitro*-p-*xylene*, a yellow powder sintering at 165°. p-*Carboxytolylarsenic acid* melts at 208°.

[With W. OBERG.]—*ψ-Cumylchloroarsine* and *ψ-cumylarsenic acid*, $C_9H_{11}AsO(OH)_2$, crystallise in white needles melting respectively at 82·5° and 224°.

p-*Cumylchloroarsine* is an oil boiling at 170° under 30 mm. pressure; p-*cumylarsenic acid* crystallises in lustrous, white needles, melts at 152°, and when oxidised by permanganate gives rise to *p*-carboxyphenylarsenic acid.

[With A. TRAEGEL.]—tert.*Butylphenylchloroarsine*, $CMe_3{\cdot}C_6H_4{\cdot}AsCl_2$, a colourless oil boiling at 175—180° under 20 mm. pressure, yields an *oxide* melting at 89°, a *sulphide* melting at 292°, and arseno*tert.*butylbenzene melting at 198°; the *acid*, $CMe_3{\cdot}C_6H_4{\cdot}AsO(OH)_2$, crystallises in needles and melts at 193°.

[With E. BÜSCHLER.]—*β-Naphthylchloroarsine*, $C_{10}H_7{\cdot}AsCl_2$, prepared from mercury-*β*-dinaphthyl, and arsenious chloride, crystallises from light petroleum in aggregates of needles melting at 69°; the *oxide* is amorphous and melts at 270°; *arseno-β-naphthalene*, $As_2(C_{10}H_7)_2$, crystallises from xylene in needles and melts at 234°. *β-Naphthylarsenic acid* crystallises from water in needles and melts at 155°. G. T. M.

Organic Chemistry.

Action of Nitrosulphuric Acid on Saturated Hydrocarbons. By Wladimir Markownikoff (*Ber.*, 1902, **35**, 1584—1587).—The author maintains, in spite of recent statements to the contrary (Zaloziecki and Frasch, *Ber.*, 1902, **35**, 386), that at the ordinary temperature nitrosulphuric acid is without action on the paraffins and polymethylenes, and that in many cases the temperature can be raised considerably without action occurring. Thus di*iso*propyl and methylpentamethylene can be distilled from the acid mixture without being changed, and dihexanaphthene, diheptanaphthene, dimenthyl, ethylnaphthene, propylnaphthene, ethylmenthane, and pure disuberyl are not affected at the ordinary temperature. When disuberyl is contaminated with suberylene or its polymerides, however, it is vigorously attacked, being partly nitrated, partly oxidised. Methyl*cyclo*hexane is only slowly acted on at 75—80°.

The author criticises the statement that dinitrobenzene and its homologues were not obtained by Zaloziecki and Frasch on nitrating the fraction of Galician petroleum boiling at 59—65°; he has often isolated dinitrobenzene from naphtha distillates of low boiling point.

W. A. D.

The Addition of Hypochlorous Acid to Propylene. By Louis Henry (*Compt. rend.*, 1902, **134**, 1070—1072).—A reply to Tiffeneau (*Compt. rend.*, 1902, **134**, 774). The author believes that the two chlorohydrins, $CH_2Cl\cdot CHMe\cdot OH$ and $OH\cdot CH_2\cdot CHMeCl$, are produced by the action of hypochlorous acid on propylene. By the action of hypochlorous acid on allylene derivatives, the hydroxyl group is, for the main part, attached to the $:CH_2$ group.

J. McC.

Aliphatic Nitro-compounds. By Heinrich Biltz (*Ber.*, 1902, **35**, 1528—1533).—When tetrachloroethylene is heated with nitrogen peroxide under pressure, a quantitative yield of tetrachlorodinitroethane is obtained (compare Kolbe, *Ber.*, 1869, **2**, 326, and Hoch, this Journal, 1873, 364); it melts and decomposes at 143—144°. *Tetrabromodinitroethane*, obtained in an analogous manner from tetrabromoethylene, crystallises from light petroleum, is soluble in alcohol or benzene, and melts and decomposes at 154—156°.

Diphenyldichlorodinitroethane, obtained when diphenyldichloroethylene is heated in a sealed tube with nitrogen peroxide for 3—4 hours at 50—60°, is a yellow, viscous oil with an odour like chloropicrin.

a-Dichlorostyrene and *aaβ*-trichlorostyrene do not form additive compounds with nitrogen peroxide.

R. H. P.

Oxidation of Tetrachloro- and Tetrabromo-ethylene. By Heinrich Biltz (*Ber.*, 1902, **35**, 1533—1537).—It is shown that when tetrachloro- and tetrabromo-ethylene are treated with a mixture of sulphuric and nitric acids according to Hoch's method (this Journal, 1873, 364), they are oxidised and converted into trichloroacetyl chloride and tribromoacetyl bromide respectively.

Tribromoacetyl bromide is a colourless oil which only reacts slowly with water.
R. H. P.

Separation of the Amyl Alcohols from Fusel Oil. III. By WILHELM MARCKWALD (*Ber.*, 1902, **35**, 1595—1601. Compare Abstr., 1901, i, 248).—The amyl alcohol obtained from molasses spirit contains a much larger proportion (48—58 per cent.) of the active alcohol than that prepared from grain or potato spirit (13·5—22 per cent.). Details are given for separating pure inactive amyl alcohol from fusel oil by fractionally crystallising the derived mixture of barium amyl sulphates; these salts crystallise together in an unbroken series of mixed crystals, and, by careful procedure, 200 grams of pure barium *iso*amyl sulphate can be obtained from 700 grams of the mixed salts. The active salt can be isolated, but with somewhat greater difficulty from the more soluble fractions.

The solubility of barium *iso*amyl sulphate in 100 parts of water is 11·85 at 19·3° and 12·15 at 20·5°; that of the corresponding active amyl salt, $(C_5H_{11}O_4S)_2Ba,2H_2O$, is 26·10 at 20·5°, $[\alpha]_D$ varying from +2·58 to +2·71 for concentrations ranging from $c=20$ to $c=4$. As the specific rotatory power of the salt is not affected by the presence of barium *iso*amyl sulphate, the composition of mixtures of the two salts can be determined from their optical activity.
W. A. D.

Preparation of Acetic Anhydride. FARBENFABRIKEN VORM. F. BAYER & CO. (D. R.-P. 127350).—Acetic anhydride is readily prepared by treating dry sodium acetate at 20° with a mixture of chlorine and sulphur dioxide in approximately molecular proportion, the latter gas being slightly in excess. The gases are rapidly absorbed, and a semi-crystalline magma is formed from which the acetic anhydride is distilled.
G. T. M.

Beryllium Compounds of the Type $Be_4O(OR)_6$. By H. LACOMBE (*Compt. rend.*, 1902, **134**, 772—774).—The action of acids of the acetic series on beryllium carbonate yields compounds of the type $Be_4O(OR)_6$, in which R is the acid radicle. The lower members are crystalline solids and the higher members are liquid; all of them volatilise without decomposing under ordinary or reduced pressure:

	Melting point.	Boiling point normal pressure.	Boiling point. under 19 mm. pressure.
Beryllium formate	sublimes without melting	—	—
,, acetate	283—284°	330—331°	sublimes without melting
,, propionate ...	119—120	339—341	221°
,, *iso*butyrate...	76	336—337	216
,, butyrate......	liquid	—	239
,, *iso*valerate...	liquid	—	254

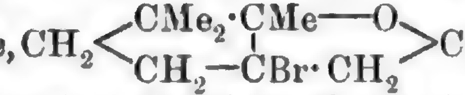
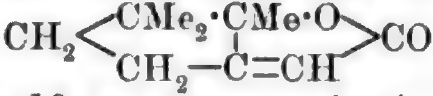
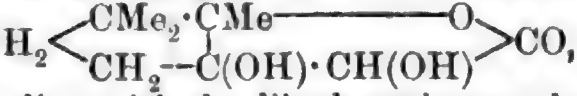
They are all insoluble in cold water, but are dissolved and decomposed by boiling water. The formate is insoluble in all organic solvents; the acetate is soluble only in chloroform, whilst the others are soluble in all ordinary solvents. In benzene, the molecular weights determined cryoscopically are lower than the calculated numbers, whilst in ethylene bromide they are higher than, but approximate fairly closely to, the calculated numbers.

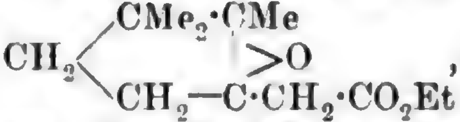
The author was unable to obtain normal beryllium salts of the acids of the acetic series, and on the other hand could not obtain inorganic salts of this special type. C. H. B.

The Fatty Oil contained in the Seeds of Lindera Benzoin. II. Lauric Acid and some of its Derivatives.

By Charles E. Caspari (*Amer. Chem. J.*, 1902, **27**, 291—311).—These seeds yield by extraction with ether 58·1 per cent., and by expression 34·5 per cent. of a yellow fat melting at 26° and soluble in alcohol, benzene, light petroleum, or acetone. The saponification number is 284·8, and the Reichert number 1·29 to 1·34. The fat consists of a mixture of the glycerides of decoic (capric), lauric, and oleic acids. The author records melting and boiling points for lauric acid and its amide and chloride differing slightly from those previously recorded by Krafft; the *anilide* forms fluffy needles melting at 76·5°, and the *o-toluidide* white needles melting at 81·5°; the barium, *strontium*, *magnesium hydrogen*, lead, manganese, zinc, and cobalt salts of lauric acid have also been prepared and their composition determined (compare Oudemans, *J. pr. Chem.*, 1863, **89**, 331). T. A. H.

Constitution of Campholenic and Nitro-campholenic Acids.

By Auguste Béhal (*Bull. Soc. Chim.*, 1902, [iii], **27**, 402—412).—By treating the lactone of β-campholenic acid with bromine, *bromocampholenolactone*,  $CH_2<\begin{matrix}CMe_2\cdot CMe—O\\ CH_2—CBr\cdot CH_2\end{matrix}>CO$, is obtained as a crystalline substance which has the odour of camphor and melts at 146°. It is very soluble in alcohol and in benzene, and soluble in twice its weight of light petroleum. When heated with aqueous or alcoholic sodium hydroxide, it yields a salt of dihydroketocampholenic acid; if alkali carbonate is employed, the lactone of the dihydroketocampholenic acid (dehydrocampholenolactone),  $CH_2<\begin{matrix}CMe_2\cdot CMe\cdot O\\ CH_2—C{=}CH\end{matrix}>CO$, which melts at 32° and boils at 193° under 19 mm. pressure, is obtained. This is unsaturated, and with bromine forms a dibromo-compound which melts at 99—100°; it is oxidised by permanganate with formation of dihydroxycampholenolactone,  $CH_2<\begin{matrix}CMe_2\cdot CMe———O\\ CH_2—C(OH)\cdot CH(OH)\end{matrix}>CO$, melting at 128°. The acid corresponding with the dihydroxylactone has not been obtained. The lactone in turn undergoes oxidation with formation of oxalic, dimethylhexanonoic, and dimethyllævulic acids, a result which is not in accord with the formula for dehydrocampholenolactone put forward by Tiemann (Abstr., 1897, i, 249). When heated under the ordinary pressure, dehydrocampholenolactone gives off carbon dioxide and an almost quantitative yield is obtained of a hydrocarbon, *didehydrocampholene*, C_9H_{14}, which boils at 127—128° under 757 mm. pressure.

When dehydrocampholenolactone is heated in a sealed tube with alcoholic ammonia, an *amide* is formed which melts at 236°. *Methyl ketocampholenate*, obtained by heating sodium ketocampholenate with methyl iodide in alcoholic solution, is a liquid which boils at 135—138° under 33 mm. pressure and has a sp. gr. 1·068 at 0°. *Ethyl ketocampholenate*,  $CH_2\left<\begin{array}{l}CMe_2\cdot CMe\\ \qquad\qquad >O\\ CH_2—C\cdot CH_2\cdot CO_2Et\end{array}\right.$, boils at 147—148° under 25 mm. pressure; *benzyl ketocampholenate* is a crystalline substance which melts at 46—47°.

The author considers that Tiemann's view that dihydroketocampholenic acid contains an ethylene oxide group should be accepted. As a consequence of the formula which the author proposes, it would follow that a tertiary alcoholic group in the γ-position relatively to a carboxyl group and having an adjoining ethylene bond has a tendency to pass into a saturated compound having an ethylene oxide grouping.

A nomenclature for the campholanes and campholenic acids and their derivatives is proposed. A. F.

Pulegenic Acid. By LOUIS BOUVEAULT and LÉON TÉTRY (*Bull. Soc. Chim.*, 1902, [iii], **27**, 307—313).—In preparing pulegenic acid by Wallach's method (Abstr., 1896, i, 309), the authors have isolated two compounds not observed by the former investigator. The first of these is a *lactone*, isomeric with pulegenic acid, which crystallises in small, transparent prisms melting at 79—80°; it is insoluble in water or sodium carbonate, but readily soluble in alkali hydroxides and in organic solvents. This lactone is formed only in very small quantities but is different from the lactone obtained by Wallach, which can be obtained by boiling pulegenic acid with dilute sulphuric acid. Another isomeride of pulegenic acid is also produced in the reaction; this is a colourless oil with neutral reaction, which boils at 113° under 21 mm. pressure, combines with bromine, and contains neither a hydroxyl nor a carbonyl group.

The authors have also prepared the *anilide* and the p-*toluidide* of pulegenic acid. The former, obtained by heating pulegenic acid with aniline for several hours at a temperature of 190—200°, crystallises from light petroleum in colourless needles melting at 123°; it is very soluble in alcohol or in ether, sparingly so in light petroleum, and is attacked by alcoholic potassium hydroxide only when heated with it in a sealed tube at above 180°. The *p*-toluidide, obtained in a similar manner to the anilide, forms slender, colourless needles which melt at 143°, is very soluble in ether, but sparingly so in light petroleum.

A. F.

Action of Organomagnesium Compounds on β-Ketonic Esters. By VICTOR GRIGNARD (*Compt. rend.*, 1902, **134**, 849—851. Compare Abstr., 1901, i, 250, 263, 393, 679, and this vol., i, 198).—In addition to small quantities of methane and hydrogen, ethyl acetoacetate and magnesium methiodide yield products from which water regenerates the unchanged ester and magnesium iodide; the ester reacts in its enolic form. From ethyl ethylacetoacetate and magnesium methiodide, the unchanged ester, and an ester, $OH\cdot CMe_2\cdot CHEt\cdot CO_2Et$, are obtained; on hydrolysis with 10 per cent. potassium hydroxide, the latter yields *β-hydroxy-β-methyl-α-ethylbutyric acid*,

$$\mathrm{OH{\cdot}CMe_2{\cdot}CHEt{\cdot}CO_2H},$$

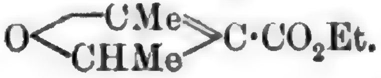
which crystallises in needles melting at 71—72°, and boils at 147° under 10 mm. pressure. If the mixture of magnesium methiodide and ethyl ethylacetoacetate is heated at 100°, a *glycol*,

$$\mathrm{OH{\cdot}CMe_2{\cdot}CHEt{\cdot}CMe_2{\cdot}OH},$$

is obtained together with unchanged ester; the former crystallises in slender needles melting at 52° and boils at 127—128° under 11 mm. pressure.

Methyl diethylacetoacetate and magnesium methiodide react at the ordinary temperature, producing methyl α-ethylbutyrate (b. p. 135—137° under 736 mm. pressure); when the two substances are heated together at 100° under pressure, a small quantity of an unsaturated hydrocarbon, C_8H_{16}, is obtained; it boils at 115—120° under 750 mm. pressure, and probably is formed by the dehydration of an alcohol, $\mathrm{CHEt_2{\cdot}CMe_2{\cdot}OH}$.

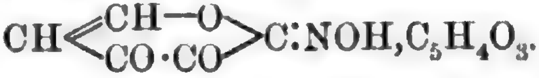
Ethyl ethylideneacetoacetate and magnesium methiodide yield a liquid which decomposes on hydrolysis with the formation of methyl *iso*butyl ketone (b. p. 113—116° under 753 mm. pressure). From this result it would appear that ethyl ethylideneacetoacetate is represented by Claisen's formula,



$$\mathrm{O}<\begin{matrix}\mathrm{CMe}\\ \mathrm{CHMe}\end{matrix}>\mathrm{C{\cdot}CO_2Et}.$$

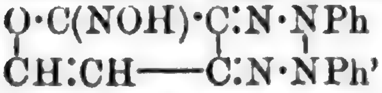
K. J. P. O.

Tautomerism of Pyromeconic Acid. By ALBERTO PERATONER (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 246—250).—It has been shown by the author and Leonardi (Abstr., 1900, i, 550) that pyromeconic acid exhibits reactions indicating both an enolic and a ketonic structure. The author now finds that the nitrosodipyromeconic acid obtained by Ost (Abstr., 1879, 708) by the interaction of nitrous and pyromeconic acids is derived from the ketonic modification, and is really an *iso*nitroso-derivative having the constitution



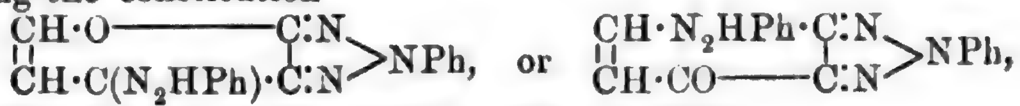
$$\mathrm{CH}<\begin{matrix}\mathrm{CH{-}O}\\ \mathrm{CO{\cdot}CO}\end{matrix}>\mathrm{C{:}NOH},C_5H_4O_3.$$

A better method than that of Ost for preparing this compound is by the action of an alkyl nitrite (ethyl nitrite giving good yields) on a chloroform solution of pyromeconic acid. The action of phenylhydrazine on this substance gives rise to a mixture of two stereoisomeric *phenylosazones* of nitrosopyromeconic acid of the composition $C_{17}H_{15}O_2N_5$; both these separate from xylene solution in yellow needles, the melting points being 165° and 197° respectively; both give yellow, slightly soluble xantho-compounds when treated with alkali, and after long boiling with hydrochloric acid they reduce Fehling's solution. On oxidation, these compounds yield the corresponding *osotetrazones*,



$$\begin{matrix}\mathrm{O{\cdot}C(NOH){\cdot}C{:}N{\cdot}NPh}\\ \mathrm{CH{:}CH{-\!-}C{:}N{\cdot}NPh}\end{matrix},$$

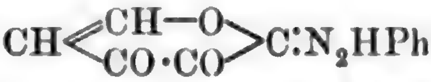
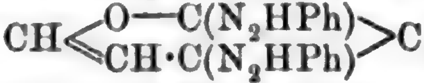
and when heated above their melting points they lose water and yield one and the same osotriazole *derivative* having the constitution



$$\begin{matrix}\mathrm{CH{\cdot}O{-\!-\!-}C{:}N}\\ \mathrm{CH{\cdot}C(N_2HPh){\cdot}C{:}N}\end{matrix}>\mathrm{NPh},\quad\text{or}\quad\begin{matrix}\mathrm{CH{\cdot}N_2HPh{\cdot}C{:}N}\\ \mathrm{CH{\cdot}CO{-\!-}C{:}N}\end{matrix}>\mathrm{NPh},$$

and separating in white needles melting at 242°.

Pyromeconic acid reacts as a keto-compound with diazonium acetate,

yielding the *phenylhydrazone*,  $\mathrm{CH}\left\langle\begin{array}{l}\mathrm{CH{-}O}\\ \mathrm{CO\cdot CO}\end{array}\right\rangle\mathrm{C{:}N_2HPh}$, which is deposited from xylene or alcohol in red needles melting and decomposing at 175° ; with excess of phenylhydrazine, this hydrazone yields a small quantity of an *isomeric* hydrazone also melting at 175°, but is mainly converted into a *triphenylhydrazone*,  $\mathrm{CH}\left\langle\begin{array}{l}\mathrm{O{-}C(N_2HPh)}\\ \mathrm{CH\cdot C(N_2HPh)}\end{array}\right\rangle\mathrm{C{:}N_2HPh}$, which crystallises from dilute acetic acid in leaflets melting at 158·5°.
T. H. P.

Study of Ethyl Glutaconate. By FERDINAND HENRICH (*Ber.*, 1902, **35**, 1663—1667. Compare Abstr., 1898, i, 631).—Ethyl glutaconate, which contains a methylene group situated between a carbonyl radicle and an unsaturated double linking, resembles ethyl acetoacetate and other substances of this type. Its *sodium* derivative, $C_9H_{13}O_4Na$, readily obtained by heating the ethereal solution of ether with sodium, has an intensely yellow colour and appears to be stable for some time in aqueous solution.

The dimethylglutaric acid, obtained by reducing dimethylglutaconic acid with phosphorus and hydriodic acid, crystallises from benzene in druses melting at 100—101°, and is not identical with the substance obtained by Blaise (*Bull. Soc. Chim.*, 1899, [iii], **21**, 623) which melted at 81°.

On condensing the unsaturated ester with acetaldehyde in the presence of diethylamine, an oily substance is obtained boiling at 150—160° under 14 mm. pressure, which gives figures approximating to the composition of *ethyl a-ethylidenediglutaconate*; the product is, however, very unstable, and decomposes even when distilled under 5 mm. pressure. In this condensation, a very small quantity of a compound is produced having the composition of ethyl a-ethylideneglutaconate, $CO_2Et\cdot CH{:}CH\cdot C(CHMe)\cdot CO_2Et$.

Potassium a-benzylideneglutaconate is prepared by condensing benzaldehyde and ethyl glutaconate in a methyl alcohol solution of potassium hydroxide ; the *acid*, $CO_2H\cdot C(CHPh)\cdot CH{:}CH\cdot CO_2H$, decomposes at 161° and is hydrolysed by dilute sulphuric acid. Similar condensation products are obtained from *p*-nitrobenzaldehyde and salicylaldehyde.

A *formazyl* derivative is produced by treating 1 mol. of ethyl glutaconate dissolved in dilute alcohol containing sodium acetate with 2 mols. of benzenediazonium chloride ; it separates from benzene and light petroleum in ruby-red crystals with a metallic lustre and melts at 117°.
G. T. M.

Some Derivatives of Ethyl Pyruvylpyruvate. By L. J. SIMON (*Compt. rend.*, 1902, **134**, 1063—1065).—The compound

$$NPh{:}CMe\cdot CO\cdot CH_2\cdot C(CO_2Et){:}NPh,$$

obtained by the action of aniline on ethyl pyruvate (Abstr., 1894, i, 509 ; 1896, i, 85), assumes a red colour when treated with sulphuric acid of sp. gr. 1·84. When the solution is poured on to ice, white crystals of the compound $NPh{:}CMe\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et$ are formed. This substance can be recrystallised from alcohol ; it melts at

139—140°, is sparingly soluble in cold water, but easily so in the ordinary organic solvents, and particularly in pyridine. It is insoluble in dilute, but soluble without change in concentrated, acids. It is easily soluble in dilute potassium hydroxide, and acids reprecipitate it from the solution; it behaves, therefore, as an acid. By prolonged action of alkali, it suffers decomposition. When dissolved in excess of alkali and heated for a few minutes, it is hydrolysed, and dilute mineral acid then precipitates the corresponding diketonic acid,

$$NPh{:}CMe{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H,$$

as a white, crystalline substance which melts at 132—133° with decomposition. The acid is insoluble in water, but soluble in alcohol. Its silver salt deposits silver on heating. The hydrazone crystallises well and decomposes at 145°.

The corresponding tolylimino-derivative,

$$C_6H_4Me{\cdot}N{:}CMe{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et,$$

resembles the phenylimino-compound; it melts at 152°.

If sulphuric acid containing 25 to 50 per cent. of dissolved anhydride be employed, no precipitate is obtained on pouring on to ice, and it is presumed that the unknown ethyl pyruvylpyruvate is produced.

J. McC.

Copper Derivative of Ethyl Oxalacetate. By WILHELM WISLICENUS and ANTON ENDRES (*Annalen*, 1902, **321**, 372—385).—*Copper ethyl oxalacetate*, $(C_8H_{11}O_5)_2Cu,H_2O$, prepared in a state of purity by slowly adding a concentrated aqueous solution of copper acetate to an alcoholic solution of ethyl oxalacetate and crystallising the product from absolute alcohol or benzene, is obtained in bright green needles melting at 155—156°. The hydrated substance, when repeatedly crystallised from benzene, loses its water of crystallisation and changes into bluish-green plates melting at 162—164°; these, however, regain their water on exposure to the atmosphere for several days.

On crystallising the copper derivative from methyl alcohol, a substitution of a methyl radicle for ethyl takes place, so that a mixed *copper* compound of diethyl and ethyl methyl oxalacetate,

$$CO_2Et{\cdot}CH{:}C(CO_2Me){\cdot}O{\cdot}Cu{\cdot}O{\cdot}C(CO_2Et){:}CH{\cdot}CO_2Et,H_2O,$$

is produced, this substance forming light green needles melting at 132—133°. This singular change does not occur with the diethyl oxalacetate itself, even on long boiling with methyl alcohol, the greater portion of the original ester being recovered; a similar negative result is obtained with the dimethyl ester and ethyl alcohol.

Prolonged boiling of the mixed copper derivative with excess of methyl alcohol leads to the production of the *copper* derivative,

$$[CO_2Et{\cdot}CH_2{:}C(CO_2Me)O]_2Cu,H_2O,$$

of ethyl methyl oxalacetate, a compound crystallising in light green needles and melting at 165—166°. At 90°, this substance becomes anhydrous, and then melts at 173—174°; it yields methyl ethyl oxalacetate (Abstr., 1894, i, 116) on treatment with dilute sulphuric acid, and methyl 1-phenyl-5-pyrazolone-3-carboxylate when condensed with phenylhydrazine; the latter reaction shows that the methyl group is attached to the oxalyl radicle.

The preceding copper compound, on prolonged boiling with absolute alcohol, is reconverted into the corresponding diethyl derivative.

The *basic copper* derivative, $OMe \cdot Cu \cdot O \cdot C(CO_2Me){:}CH \cdot CO_2Et$, produced by boiling the anhydrous copper derivative of diethyl oxalacetate with a solution of sodium methoxide in absolute methyl alcohol, crystallises from this solvent in slender blue needles decomposing gradually above 200°. In the presence of water, this reaction takes another course, and a bluish-green, slimy precipitate containing both sodium and copper is obtained, which on treatment with acid yields the acid ester, $CO_2Et \cdot CH_2 \cdot CO \cdot CO_2H$, a substance melting at 102—103°, and not at 97—98° as previously stated (*Annalen*, 1888, **246**, 323). The formation of a basic copper derivative is not observed when alcohol and sodium ethoxide are employed.

The preceding basic copper compound is extremely soluble in benzene. This solution on prolonged boiling turns green, and after concentration deposits the neutral copper derivative of the methyl ethyl ester.

The anhydrous copper derivative of dimethyl oxalacetate, when boiled with methyl alcohol, yields a blue *basic copper* compound,

$$OMe \cdot Cu \cdot O \cdot C(CO_2Me){:}CH \cdot CO_2Me,$$

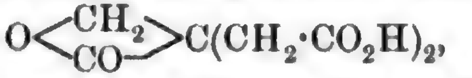
separating in slender needles and dissolving in benzene with the regeneration of the neutral substance.

The neutral copper derivative, on prolonged boiling with ethyl alcohol, gives rise to a mixed *copper* compound,

$$CO_2Me \cdot CH{:}C(CO_2Et) \cdot O \cdot Cu \cdot O \cdot C(CO_2Et){:}CH \cdot CO_2Me.$$

G. T. M.

Methylenecitric Acid. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 129255).—*Methylenecitric acid*,



$$O{<}\begin{matrix}CH_2\\CO\end{matrix}{>}C(CH_2 \cdot CO_2H)_2,$$

prepared either by heating citric acid with paraformaldehyde at 140—160° or by condensing the acid with formaldehyde solution in the presence of hydrochloric or sulphuric acid, is sparingly soluble in cold water, but readily dissolves in the hot solvent; it melts at 208° and is stable towards acids, but decomposed by alkali hydroxides and carbonates. G. T. M.

***l*-Xylonic Acid.** By CARL NEUBERG (*Ber.*, 1902, **35**, 1473—1475. Compare this vol., ii, 417).—*Brucine* l-*xylonate*, $C_5H_{10}O_6,C_{23}H_{26}O_4N_2$, prepared by neutralising an aqueous solution of the acid with brucine, crystallises in needles or rhombic plates melting at 172—174°, and has $[\alpha]_D$ $-37.65°$ at 15° in aqueous solution; l-xylonic acid is readily separated from the other products of the hydrolysis of proteids in the form of this salt (*loc. cit.*). The *cinchonine* salt crystallises in elongated plates or needles melting and decomposing at 180°, and has $[\alpha]_D$ 125·0° at 17° in aqueous solution; the *morphine* salt forms ill-defined needles melting at 153°. The *phenylhydrazide*, $C_5H_9O_5 \cdot N_2H_2Ph$, crystallises in colourless needles melting and decomposing at 129°.

K. J. P. O.

Formation of Aldehydes and Ketones from β-Chloroalcohols. By K. Krassusky (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 287—315).—In a previous paper (this vol., i, 261), the author gave a scheme for the reactions occurring in the formation of aldehydes and ketones from haloid derivatives of olefines, according to which the first product formed is a halogen derivative of an alcohol. To test the truth of this assumption, an examination has been made of the products obtained by heating β-chloro-alcohols with water and the results are in accord with it.

Trimethylethylene chlorohydrin, when heated in a sealed tube with water, reacts as follows: $OH\cdot CMe_2\cdot CHMeCl = CHMe_2\cdot COMe + HCl$, and possibly also to a certain extent according to the equation: $CMe_2Cl\cdot CHMe\cdot OH = CHMe_2\cdot COMe + HCl$. Other compounds studied were: Ethylene chlorohydrin, which is decomposed as follows: $OH\cdot CH_2\cdot CH_2Cl = CH_3\cdot CHO + HCl$; propylene chlorohydrin, which splits up in two ways, $OH\cdot CHMe\cdot CH_2Cl = COMe_2 + HCl$ and $OH\cdot CHMe\cdot CH_2Cl = CH_2Me\cdot CHO + HCl$; *iso*butylene chlorohydrin, $OH\cdot CMe_2\cdot CH_2Cl = CHMe_2\cdot CHO + HCl$; hexylene chlorohydrin, which gives a ketone and hydrogen chloride; tetramethylethylene chlorohydrin, $OH\cdot CMe_2\cdot CMe_2Cl = CH_3\cdot CO\cdot CMe_3 + HCl$.

ψ-Butylene chlorohydrin, $OH\cdot CHMe\cdot CHMeCl$, prepared by the action of hypochlorous acid on ψ-butylene, boils at 136—137° under 760 mm. pressure and has the sp. gr. 1·0868 and 1·0870 at 0°/0° and 1·0692 at 18°/0°. When treated with water, it decomposes according to the equation: $OH\cdot CHMe\cdot CHMeCl = CH_3\cdot CO\cdot CH_2Me + HCl$.

These chlorohydrins also split up in a similar manner when they are heated alone in sealed tubes.

On heating with water in presence of lead oxide, silver oxide, or zinc oxide, these chlorohydrins yield organic oxides, and these the author considers to be the primary product, the formation of glycols, aldehydes, or ketones being the result of the action of hydrochloric acid on the organic oxides. This secondary action the author is now investigating.

T. H. P.

Apiose, a β-Hydroxymethylerythrose. By Eduard Vongerichten (*Annalen*, 1902, **321**, 71—83. Compare Abstr., 1901, i, 646).—When oxidised with bromine in aqueous solutions, apiose, the pentose derived from apiin, gives rise to a new tetrahydroxyvaleric acid to which the name *apionic acid* is given.

The *calcium* salt, $(CaC_5H_9O_6)_2$, of this acid is amorphous, the *strontium* salt, $Sr(C_5H_9O_6)_2$, is crystalline. The acid itself is a colourless syrup which yields a *phenylhydrazide*, $C_{11}H_{16}O_5N_2$, crystallising in small, white prisms melting at 126—127°.

The reduction of apionic acid with red phosphorus and hydriodic acid leads to the production of *iso*valeric acid, this substance being identified by means of its silver, calcium, and barium salts.

These results show that apiose is a β-hydroxymethylerythrose, the proof of its constitution being summarised in the following diagram:

$$COH\cdot CH(OH)\cdot C(OH)(CH_2\cdot OH)_2 \text{ (apiose)} \rightarrow$$
$$CO_2H\cdot CH(OH)\cdot C(OH)(CH_2\cdot OH)_2 \text{ (apionic acid)} \rightarrow CO_2H\cdot CH_2\cdot CHMe_2$$
(*iso*valeric acid).

G. T. M.

Acetyl Derivatives of the Two Methylglucosides; Acetylbromodextrose. By J. MOLL VAN CHARANTE (*Rec. Trav. Chim.*, 1902, [ii], **21**, 42—44).—Tetra-acetyl-α-methylglucoside (Koenigs and Knorr, Abstr., 1901, i, 369; Fischer and Armstrong, *ibid.*, 257) crystallises from benzene with $1C_6H_6$, which it loses on standing in the air; in solution in benzene, it has $[\alpha]_D$ +173°17′ at 20°, whereas the benzene-free substance in alcohol has $[\alpha]_D$ +137°17′ at 20°. Tetra-acetyl-β-methylglucoside does not crystallise with benzene, and in alcoholic solution has $[\alpha]_D$ −27°20′ at 20°.

For the preparation of acetylbromodextrose, the author finds it best to extract the mixture obtained on heating dextrose and acetyl bromide, thoroughly with water and dilute aqueous sodium carbonate, and finally to crystallise the product from ether, whence it separates in hard needles (m. p. 88—89°). K. J. P. O.

Extraction of Reducing Sugars (Monoses). By CHARLES TANRET (*Bull. Soc. Chim.*, 1902, [iii], **27**, 392—398).—For the purpose of separating and identifying monoses when mixed with hydrolysable sugars, the author recommends the conversion of the sugars into their phenylhydrazones and the separation of these by means of their varying solubilities in ethyl acetate. Thus the phenylhydrazones of lactose and maltose are only slightly soluble in ethyl acetate, whilst those of dextrose and lævulose are fairly readily soluble; it has therefore been found possible to separate from a mixture of these 77—92 per cent. of the monoses.

The author has studied the action of phenylhydrazine on several of the monoses with the view of ascertaining the amount of phenylhydrazones formed under certain conditions and their solubilities, and has prepared *arabinose phenylhydrazone* for the first time. This forms slender, white needles, melts at 153°, and is feebly dextrorotatory.

A. F.

The Swelling and Solution of Starch by Chloral Hydrate and the Influence of Chloral Hydrate on the Retardation or Prevention of the Iodine Starch Reaction. By RICHARD MAUCH (*Arch. Pharm.*, 1902, **240**, 166—178. Compare this vol., i, 344).—Solutions of chloral hydrate only cause starch to swell and dissolve when they contain 40—70 per cent. of chloral hydrate; an 80 per cent. solution does not act in this way until a temperature of nearly 100° is reached. The solution contains amylodextrin and amylogen, traces of dextrin at most, and no dextrose. The different kinds of starch behave in somewhat different ways.

A solution of starch in chloral hydrate solution reacts comparatively slowly with iodine, and does not react at all when the percentage of chloral hydrate present exceeds 70. A solution of iodine in 80 per cent. chloral hydrate solution does not colour dry starch grains, solutions containing 70 per cent. or less of chloral hydrate do colour the grains.

A list of cases is given in which a 60—80 per cent. aqueous solution of chloral hydrate may be employed advantageously in analysis. C. F. B.

Transformation of New Bread into Old. By LÉON LINDET (*Compt. rend.*, 1902, **134**, 908—910).—When bread is allowed to become stale, the only change occurring in the crust is one of hydration; there is no alteration in the proportion of soluble dextrin, and the starch present is as capable of absorbing water after 48 hours as when the loaf is taken out of the oven. On the other hand, very marked changes take place in the composition of the crumb, the percentage of soluble amylodextrin falls from 10 to 2 per cent.; the starch becomes less soluble in dilute acid and less capable of absorbing water; these chemical changes correspond with the increase in the friability of the crumb.

The communication includes a table of numerical data referring to the estimation of the dextrin and insoluble starch and the ratio between the volumes of the latter substance before and after hydration; this quantity, which is taken to be the coefficient of absorption, is constant for the crust but falls from 6·7 to 2·8 for the crumb.

G. T. M.

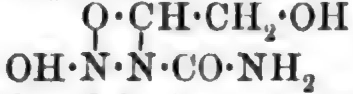
[Attempt to prepare] Derivatives of Methylenediamine. By RICHARD KUDERNATSCH (*Monatsh.*, 1902, **23**, 119—122).—Methylene chloride does not react with benzenesulphonethylamide, and with its sodium derivative only in the complete absence of water and alcohol. No diethylmethylenediamine could be obtained. The product on treatment with concentrated hydrochloric acid yielded methylamine hydrochloride, and on distillation phenyl disulphide and a residue which on warming with alkali gave only a weak amine odour.

G. Y.

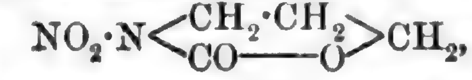
Nitroamino-alcohols. By ANTOINE P. N. FRANCHIMONT and A. LUBLIN (*Rec. Trav. Chim.*, 1902, **21**, 45—55).—A more detailed account of work previously published (Abstr., 1901, i, 674).

Ethyl β-hydroxyethylaminoformate (β-hydroxyethylcarbamate) boils at 152° under 12 mm., and at 163° under 16 mm. pressure.

The character of hydroxyethylnitrocarbamide (*loc. cit.*) suggests that it is more appropriately represented by the formula



$$\begin{array}{l}\quad\ \mathrm{O{\cdot}CH{\cdot}CH_2{\cdot}OH} \\ \mathrm{OH{\cdot}N{\cdot}N{\cdot}CO{\cdot}NH_2}\end{array}$$

The internal anhydride of hydroxypropylcarbamic acid is prepared from bromopropylphthalimide, and on nitration yields 2-*keto*-1-*nitropentoxazolidine*,  $\mathrm{NO_2{\cdot}N}<\begin{array}{c}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CO{-}{-}O}\end{array}>\mathrm{CH_2}$, which crystallises in colourless leaflets melting at 74°; when boiled with water, it decomposes into carbon dioxide and an oily substance. K. J. P. O.

Improved Method for the Preparation of Betaine. By VL. STANĚK (*Zeit. Zuckerind. Böhm.*, 1902, **26**, 287—289).—Concentrated sulphuric acid, when heated with betaine for 5 hours at 120°, or for 3 hours at 130°, has but slight action on it, whilst under the same conditions sucrose and asparagine undergo complete decomposition. The author's method, based on this marked stability of betaine, is as follows: Equal quantities of either molasses or osmose liquors of sp. gr. 85° Baumé from the manufacture of beet sugar and concentrated sulphuric acid are mixed in a large flask, and when the first violent reaction is over the mass is heated at 120—130° for 3 hours, then stirred up with water and made alkaline with calcium hydroxide. The liquid is then evaporated to dryness and the powdered residue repeatedly extracted with boiling alcohol, by which means almost the whole of the betaine is brought into solution. After boiling with spodium, the liquid is filtered and the alcohol distilled off. The residual solution may then be well cooled and treated with a current of hydrogen chloride, or it may be evaporated to a syrup to deposit betaine, which is removed, the mother liquor, after dilution with double its volume of alcohol, being then treated with hydrogen chloride. The betaine hydrochloride obtained in either of these ways is recrystallised from water or dilute alcohol. Satisfactory yields are obtained by this method. T. H. P.

Betaine Aurichloride. By EMIL FISCHER (*Ber.*, 1902, **35**, 1593—1595).—Contrary to Willstätter's statement (this vol., i, 266), betaine aurichloride is partially decomposed when crystallised from water, and can only be obtained pure by crystallisation from dilute hydrochloric acid; it then melts, when rapidly heated, at 245° (250° corr.), not at 209°. W. A. D.

Products of Decomposition of Aminotariric Acids. By ALBERT ARNAUD (*Compt. rend.*, 1902, **134**, 842—843. Compare this vol., i, 342, 343).—The oxime of ketotariric acid (*loc. cit.*) yields a mixture of two aminotariric acids (denoted as α and β) when heated with concentrated sulphuric acid at 100°. This mixture crystallises in white needles melting at 75—76°, and when heated under pressure at 170° with fuming hydrochloric acid gives four substances. *α-Aminotariric acid*, $C_{11}H_{23}\cdot NH\cdot CO\cdot[CH_2]_5\cdot CO_2H$, breaks up into undecylamine, $C_{11}H_{23}\cdot NH_2$ and pimelic acid, $C_5H_{10}(CO_2H)_2$; whereas *β-aminotariric acid*, $C_{11}H_{23}\cdot CO\cdot NH\cdot[CH_2]_5\cdot CO_2H$, yields lauric acid, $C_{11}H_{23}\cdot CO_2H$, and ε-aminohexoic acid, $NH_2\cdot[CH_2]_5\cdot CO_2H$. These reactions are in accordance with the formula,

$$CH_3\cdot[CH_2]_{10}\cdot C⋮C\cdot[CH_2]_4\cdot CO_2H,$$

previously suggested for tariric acid (*loc. cit.*). K. J. P. O.

Sulphamides and Sulphanilides of the Aliphatic Series. By DUGUET (*Rec. Trav. Chim.*, 1902, [ii], **21**, 75—86).—*Propylsulphonic chloride*, $CH_2Me\cdot CH_2\cdot SO_2Cl$, prepared from potassium propylsulphonate and phosphorus pentachloride, is a mobile liquid which boils at 77·5—78° under 13 mm., and at 180° with decomposition under ordinary pressure, and has a sp. gr. 1·2996 at 0°/4°; in dry ethereal solution, with dry ammonia, it gives *propylsulphonamide*, which crystallises in long prisms or leaflets melting at 52°; the corresponding *anilide* melts at −10°.

*iso*Butylsulphonic chloride boils at 79·5—80° and *iso*amylsulphonic chloride at 97·5—98° under 13 mm. pressure. iso*Butylsulphonamide*, $C_4H_9\cdot SO_2\cdot NH_2$, melts at 14—16°; iso*butylsulphonanilide* crystallises in white needles melting at 38—38·5°. iso*Amylsulphonamide* melts at 3°, and the corresponding *anilide* at 42°.

Methylsulphon-amide and -anilide melt respectively at 90° and 99°, and ethylsulphonanilide melts at 58°. K. J. P. O.

Bromalchloralcarbamide. KALLE & Co. (D.R.-P. 128462).—Carbamide, when mixed with molecular proportions of chloral and bromal or when heated with the corresponding quantities of their hydrates in the presence of concentrated hydrochloric or sulphuric acid, yields *bromalchloralcarbamide*,

$$CBr_3\cdot CH(OH)\cdot NH\cdot CO\cdot NH\cdot CH(OH)\cdot CCl_3,$$

a substance separating in small crystals, decomposing at 186° and dissolving readily in ether or the alcohols. The solution of this compound in sodium or potassium hydroxide evolves bromoform and chloroform on gently warming, or even when left at the ordinary temperature. Neutral silver nitrate solution has no action on the compound, even on boiling, but the ammoniacal solution is immediately reduced.

G. T. M.

Composition of Commercial Potassium Cyanide. By RUSSELL W. MOORE (*J. Soc. Chem. Ind.*, 1902, **21**, 392—393).—Out of 85 samples of potassium cyanide of various brands, only 24 were free from sodium cyanide, whilst one was entirely composed of that salt. In the other samples, the percentage of sodium cyanide varied from 9·84 to 54·49. W. P. S.

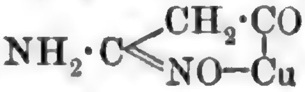
Ferrocyanides of Cadmium. By EDMUND H. MILLER (*J. Amer. Chem. Soc.*, 1902, **24**, 226—234).—It has been shown (Miller and Fisher, Abstr., 1900, ii, 761) that the results obtained on titrating neutral or slightly acid solutions of cadmium with potassium ferrocyanide do not agree with any of the formulæ given for the precipitate, whilst the values obtained with an ammoniacal solution agree closely with those required for the formula $K_2CdFe(CN)_6$. A study has been made of the composition of the precipitate obtained under various conditions.

When the ferrocyanide is in excess, the precipitate from either an ammoniacal or acid solution has the composition $K_2CdFe(CN)_6$, whilst that obtained from a neutral solution contains a larger proportion of cadmium.

When the cadmium is in excess, the composition of the precipitate formed in a neutral solution or in presence of hydrochloric acid corresponds with $K_8Cd_{10}[Fe(CN)_6]_7$, whilst in a solution containing acetic acid it corresponds with $K_6Cd_7[Fe(CN)_6]_5$.

If, in an ammoniacal solution with cadmium in excess, the suspended precipitate is decanted from that which has subsided, the former has the composition $K_2CdFe(CN)_6$, and the latter $K_2Cd_3[Fe(CN)_6]_2$; by repeatedly washing the precipitate $K_2Cd_3[Fe(CN)_6]_2$ with strong ammonia, a residue is obtained of the composition $Cd_2Fe(CN)_6$. These experiments show that the original precipitate is a mixture of two simple ferrocyanides, $Cd_2Fe(CN)_6$ and $K_2CdFe(CN)_6$. Similar examination of the precipitates obtained from acid solutions indicate that these are also mixtures (or very easily decomposable double salts) of the same two ferrocyanides. E. G.

Reactions of Amidoximes. By HUGO SCHIFF (*Annalen*, 1902, **321**, 357—371).—The substance obtained by hydrolysing oxamethane with hydroxylamine (Schiff and Monsacchi, Abstr., 1896, i, 209), and reinvestigated by Hollemann (Abstr., 1897, i, 23), is now considered to be aminoximino-oxalic acid, $OH\cdot N\colon C(NH_2)\cdot CO_2H$; it is very slightly acid until the basic function of the amino-radicle has been masked by formaldehyde (compare this vol., i, 85), after which it behaves as a monobasic acid, this reaction being due entirely to the carboxyl group, and not to the *iso*nitroso-radicle.

Amino-oximinomalonic acid, $OH\cdot N\colon C(NH_2)\cdot CH_2\cdot CO_2H$ (Modeen, Abstr., 1892, i, 139, and Pinner and Oppenheimer, Abstr., 1895, i, 266), also behaves as a monobasic acid in the presence of formaldehyde; its *copper* salt,  $NH_2\cdot C\begin{matrix} \diagup CH_2\cdot CO \\ \diagdown NO-Cu \end{matrix}$, is a dark green, granular substance.

Hydroxamoximinomalonic acid, $OH\cdot N\colon C(NH\cdot OH)\cdot CH_2\cdot CO_2H$ (Hantzsch and Urbahn, Abstr., 1895, i, 393), behaves as a dibasic acid, the acid character being due to the carboxyl and *iso*nitroso-groups; the addition of formaldehyde to the neutralised solution causes the mixture to become alkaline; this exceptional behaviour is probably due to the removal of the alkali radicle from the oxime group, owing to the interaction of the latter with formaldehyde. The free acid melts at 144—145° (compare Hantzsch and Urbahn, *loc. cit.*), and yields a green *copper* salt, $Cu[O\cdot N\colon C(NH\cdot OH)\cdot CH_2\cdot CO_2\cdot Cu\cdot OH]_2$.

The formation of the flocculent, green copper derivatives is a characteristic property of the amino-oximes, and the communication contains a summary of the compound of this type giving distinctive reactions with copper salts.

Oximinolactamide, $OH\cdot CHMe\cdot C(NH_2)\colon N\cdot OH$, and the succeeding amino-oximes are all obtained by treating the corresponding cyanohydrins with hydroxylamine hydrochloride and sodium carbonate in aqueous solutions; it crystallises from ethyl acetate in colourless plates melting at 115—116°; its *benzoyl* derivative melts at 188—189°.

Oximino-α-hydroxyhexoamide, $CHMe_2\cdot CH_2\cdot CH(OH)\cdot C(NH)_2\colon NOH$, produced from *iso*valeraldehyde cyanohydrin, crystallises from water or ether, melts at 176·5°, and yields a green copper derivative.

Oximino-α-hydroxyoctoamide, $C_6H_{13}\cdot CH(OH)\cdot C(NH_2)\colon NOH$, derived from œnanthaldehyde cyanohydrin, separates from dilute methyl alcohol in leaflets melting at 141°, the *benzoyl* derivative melts at 143°.

Oximino-α-hydroxybutyramide, $OH\cdot CMe_2\cdot C(NH_2)\colon N\cdot OH$, prepared from acetone cyanohydrin, ammonium hypochlorite, and ammonium or sodium carbonate, crystallises from anhydrous ether in colourless needles melting at 51—52° and subliming at 55—60°; it gives an intense reddish-violet coloration with alkaline copper solutions. The amino-oxime is, however, very unstable, and after six months loses this characteristic property.

Oximinotrichlorolactamide, $CCl_3\cdot CH(OH)\cdot C(NH_2)\colon NOH$, melts at 156—157° and not at 145° (compare Richter, Abstr., 1892, 321); it forms a *green* copper derivative, $C_3H_3O_2N_2Cl_3(Cu\cdot OH)_2$.

G. T. M.

Transformation of Nitro-derivatives into Hydroxamic Acids. By C. Ulpiani and C. Ferretti (*Gazzetta*, 1902, **32**, i, 205—217).—The action of concentrated sulphuric acid on nitromalonamide yields two products: (1) a small quantity of a white, crystalline *compound*, $C_2H_2O_2N_2$, melting at 216° and slightly soluble in water or alcohol; (2) a compound, $C_2H_4O_3N_2$, identical with that obtained by Schiff and Monsacchi (Abstr., 1896, i, 209), which the author shows to be the stable form of hydroxamic acid, formed according to the scheme:

$$NH_2\cdot CO\cdot CH(NO_2)\cdot CO\cdot NH_2 \qquad NO_2\cdot CH_2\cdot CO\cdot NH_2 \rightarrow$$
$$OH\cdot NO{:}CH\cdot CO\cdot NH_2 \rightarrow OH\cdot C(NOH)\cdot CO\cdot NH_2.$$

Its *ammonium* and *mercury* salts were prepared and analysed. On hydrolysis, the acid yields oxamic acid, oxalic acid, and ammonium hydrogen oxalate. See also Holleman (Abstr., 1897, i, 23).

T. H. P.

Hydroxy*iso*propylphosphinic Acid. By CH. MARIE (*Compt. rend.*, 1902, **134**, 847—849. Compare Abstr., 1901, i, 635, and this vol., i, 255).—*Hydroxyisopropylphosphinic acid* (H_3PO_3,C_3H_6O) is most conveniently prepared from hydroxy*iso*propylhypophosphorous acid (*loc. cit.*), which is oxidised in aqueous solution by a slight excess of mercuric chloride. After removing the excess of mercuric salt by hydrogen sulphide, and the hydrochloric acid by evaporation, the acid is purified by recrystallisation from acetic acid. Other oxidising agents may be used, but hydroxy*iso*propylhypophosphorous acid cannot be oxidised electrolytically.

Hydroxy*iso*propylphosphinic acid forms small, white crystals, melting at 175° (compare *loc. cit.*), which are stable in the air. It slowly decomposes at 150—160°, but only completely at 250°. Prolonged ebullition with hydrochloric acid slowly converts it into acetone and phosphorous acid; boiling alkali hydroxides are without effect. In the presence of methyl orange, it behaves as a monobasic acid, but in the presence of phenolphthalein as a dibasic acid. It is not a reducing agent. Its calcium, barium, and strontium salts are crystalline, and more soluble in cold than in hot water. The silver and lead salts are insoluble crystalline precipitates.

K. J. P. O.

Salts of Hydroxy*iso*propylphosphinic Acid. By CH. MARIE (*Compt. rend.*, 1902, **134**, 994—995).—Hydroxy*iso*propylphosphinic acid (preceding abstract), gives normal and hydrogen salts. The normal *sodium* salt, $Na_2HPO_3,C_3H_6O,5H_2O$, is obtained as crystals which lose water at 100° and decompose at 210—220°; it is extremely soluble in water, and is not precipitated by alcohol. The *sodium hydrogen* salt, $NaH_2PO_3,C_3H_6O,6H_2O$, is prepared by neutralising the acid with sodium hydroxide (using methyl-orange as indicator) and precipitating with alcohol; the salt effloresces and loses its water completely at 100°. At this temperature also acetone is evolved and the decomposition takes place according to the equation: $2NaH_2PO_3,C_3H_6O = Na_2H_2P_2O_5,C_3H_6O + H_2O + C_3H_6O$. When the normal sodium salt is treated with a solution of a lead salt, it gives a precipitate of $PbHPO_3,C_3H_6O$, which is sparingly soluble in water but very easily soluble in nitric acid. On treating the free acid with excess of copper carbonate and precipitating with alcohol, the compound $Cu(H_2PO_3,C_3H_6O)_2,2C_2H_6O$ is obtained; this loses its alcohol slowly at the ordinary temperature and rapidly at 100°, giving $Cu(H_2PO_3,C_3H_6O)_2$.

The *copper hydrogen* salt with alcohol of crystallisation, when dissolved in warm water, decomposes, alcohol being evolved and the normal salt, $CuHPO_3,C_3H_6O,H_2O$ precipitated; this loses water completely at 150°. The *silver* salt, Ag_2HPO_3,C_3H_6O, is obtained as white, stable crystals by precipitation. Attempts to prepare a silver hydrogen and a lead hydrogen salt have invariably led to the production of the normal salts.

J. McC.

Cacodylic Acid and its Compounds. By GIUSEPPE SIBONI (*Chem. Centr.*, 1902, i, 744; from *Boll. Chim. Farm.*, 41, 73—82).—The sodium, potassium, lithium, silver, calcium, barium, mercury, and iron salts of cacodylic acid are described in the original paper, together in some cases with details of their preparation and of methods of testing them. The commercial sodium salt usually contains $2—3H_2O$. The ferrous salt is easily converted into the ferric salt; its solutions give a green coloration with citric acid which is not affected by evaporation, and the residue, after removing the citric acid by absolute alcohol, gives the reactions of ferrous and ferric salts. *Codeine cacodylate*, $AsMe_2O \cdot OH,C_{18}H_{21}O_3N$, prepared by treating barium cacodylate with an excess of codeine sulphate, forms a rather hygroscopic, reddish-white, crystalline powder, and is very readily soluble in water or alcohol, but only slightly so in ether; its solutions are neutral to phenolphthalein, but alkaline to helianthin and litmus. By the action of potassium permanganate, it gradually becomes yellow, and ultimately forms a brown precipitate; with copper sulphate, it slowly gives a bluish-white precipitate in the cold, but with hot solutions the precipitate is formed immediately. Codeine cacodylate gives the codeine reaction with sulphuric acid and ferric chloride, and with ferrous sulphate solutions a bluish-green precipitate is obtained. The therapeutic application of the salts of cacodylic acid and their compounds, and the various methods of using them, are also discussed in the original paper.

E. W. W.

Oxidation of the Methyl Groups of Aromatic Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 127388).—Nickelic or cobaltic oxide may be employed in oxidising toluene, the xylenes, or nitrotoluene to the corresponding aldehyde and acid, the yield of the latter product being diminished by performing the operation in the presence of a nickel salt or of a small amount of acid.

Toluene, when heated at 100° with dry nickelic oxide, yields benzaldehyde; *o*-nitrotoluene, when mixed with the oxide and nickelous chloride and distilled in a current of steam, yields a distillate containing *o*-nitrobenzaldehyde and unaltered substance; the residue contains *o*-nitrobenzoic acid. The nickelous oxide resulting from this action is continuously reconverted into the higher oxide by slowly adding to the heated mixture a 10 per cent. solution of sodium hypochlorite.

G. T. M.

***s*- and *as*-Triethylbenzene.** By AUGUST KLAGES (*J. pr. Chem.*, 1902, [ii], 65, 394—400. Compare Abstr., 1899, i, 598).—To separate *s*-triethylbenzene from *as*-triethylbenzene, the mixture is sulphonated and warmed with phosphoric acid, when *s*-triethylbenzenesulphonic acid is decomposed into the hydrocarbon and sulphuric acid, the *as*-triethylbenzenesulphonic acid remaining unchanged. s-*Triethylbenzenesulphonic acid* is an oil; it forms a *sodium* salt, which is soluble in water or ether and is decomposed into the hydrocarbon and sodium sulphate by treatment with alcohol or by heating at 80°. The *chloride* boils at 183° under 25 mm. pressure, and has the sp. gr. 1·146 at 25°; the *amide* crystallises in colourless needles melting at 118·5°, and the *anilide* separates from dilute alcohol in brittle needles melting at 128°. s-*Triethyliodobenzene*, prepared by Klages and Liecke's method (Abstr., 1900, i, 387), is a colourless oil, which boils at 149—150° under 12 mm. pressure and has the sp. gr. 1·44 at 15°.

as-Triethylbenzene, obtained by heating the sodium sulphonate with hydrochloric acid at 140°, is a colourless oil which boils at 216—218°. The sulphonic acid forms a *barium* salt, an insoluble *magnesium* salt, a *chloride*, which is an oil boiling at 202—204° under 32 mm. pressure and has sp. gr. 1·183 at 25°, an *amide*, which forms glistening needles melting at 111°, and an *anilide*, which crystallises in rhombic plates melting at 108°. G. Y.

Methoethenylbenzene [β-Allylbenzene]. By MARC TIFFENEAU (*Compt. rend.*, 1902, **134**, 845—847).—Methoethenylbenzene [β-allylbenzene; *as*-phenylmethylethylene], $CH_2:CMePh$, is formed in small amount when phenyldimethylcarbinol is heated at its boiling point; on dehydrating the carbinol with acetic anhydride or anhydrous oxalic acid, a mixture is obtained from which the hydrocarbon can be isolated by fractionation and treatment with sodium. β-Allylbenzene is an oil boiling at 160—162°, and has a sp. gr. 0·9231 at 0°; it is quantitatively converted into *iso*propylbenzene by sodium and boiling alcohol. By aqueous potassium permanganate, it is oxidised to acetophenone and acetic and formic acids. It forms a *dibromide*, which is an oil boiling at 115° under 8 mm. pressure. By potassium acetate, the dibromide is converted into an unsaturated *monobromide*, C_9H_9Br, but when boiled with water and barium carbonate, a *glycol* is obtained, melting at 37—38° and identical with that formed by the action of magnesium methiodide on benzylcarbinol or on benzylcarbinyl acetate. The glycol is converted by sulphuric acid into β-phenylpropaldehyde, the *semicarbazone* of which melts at 203—204° The iodohydrin, obtained from β-allylbenzene by the action of iodine and mercuric oxide, is converted by silver nitrate into benzyl methyl ketone, a transformation in which the phenyl group wanders from the β- to the α-carbon atom. K. J. P. O.

Chemical Action of Light. III. By GIACOMO L. CIAMICIAN and PAUL G. SILBER (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 277—284. Compare Abstr., 1901, i, 329 and 390).—A solution of 60 grams of nitrobenzene in 200 c.c. of absolute alcohol was exposed to the action of light during the whole summer, after which 50 grams of unaltered nitrobenzene was recovered, the remaining compounds yielding 6·6 grams of a mixture of hydrochlorides. From the latter were separated:

quinaldine; a small quantity of aniline admixed with another substance which on boiling with acetic anhydride gave a compound melting at 174—175°; a tertiary *base* giving a picrate melting at 168—169°; a small quantity of an aldehydic substance. The primary reaction between the nitrobenzene and alcohol probably yields aniline and acetaldehyde, the latter, by its condensation and its reaction with aniline, then giving rise to the other products found.

m-Nitrotoluene (10 grams in 50 c.c. of absolute alcohol) yielded the corresponding methylquinaldine and *m*-toluidine; the other nitrotoluenes give similar products. No appreciable quantity of basic substances could be obtained from *o*- and *m*-dinitrobenzenes, the three nitroanilines or nitronaphthalene.

o-Nitropiperonaldehyde in benzene solution yields *o*-nitrosopiperonylic acid by molecular rearrangement; *o*-nitrocinnamaldehyde remains unchanged.

In benzene solution, *o*-nitrosobenzoic acid does not undergo change, but *o*-nitrobenzaldehyde yields a considerable proportion of *o*-nitrosobenzoic acid. In methyl or ethyl alcoholic solution, however, *o*-nitrobenzaldehyde or ethyl *o*-nitrosobenzoate yields a complex mixture of products, among which are *o*-azoxybenzenedicarboxylic acid and its diethyl ester and probably traces of ethyl anthranilate.

The transformation of *o*-nitrobenzaldehyde in alcoholic solution under the action of light takes place mainly according to the following scheme:

$$\begin{tikzcd} {} & NO_2\cdot C_6H_4\cdot CHO \arrow[r] & NO_2\cdot C_6H_4\cdot CH(OEt)\cdot OH \\ & & NO_2\cdot C_6H_4\cdot CO_2Et \\ {} \arrow[r] & NO\cdot C_6H_4\cdot CO_2Et \arrow[ur] \arrow[dr] & \\ & & ON_2(C_6H_4\cdot CO_2Et)_2 \end{tikzcd}.$$

T. H. P.

Preparation and Nitration of Derivatives of Toluene-*p*-sulphonic Chloride. By Frédéric Reverdin and Pierre Crépieux (*Ber.*, 1902, **35**, 1439—1444).—*Toluene*-p-*sulphon*-o-*toluidide*,

$$C_6H_4Me\cdot SO_2\cdot NH\cdot C_6H_4Me,$$

crystallises from dilute acetic acid in white needles and melts at 108°. The *mononitro*-derivative crystallises from dilute acetic acid in yellow needles and melts at 174°; it is hydrolysed to 5-nitro-1:2-toluidine. Other nitro-derivatives in the mother liquor gave on hydrolysis 3-nitro-1:2-toluidine and 3:5-dinitro-1:2-toluidine.

By the action of nitric acid on toluene-*p*-sulphon-*p*-toluidide, the *nitro*-derivative, $C_6H_4Me\cdot SO_2\cdot NH\cdot C_6H_3Me\cdot NO_2$ [$Me:NH:NO_2 = 1:4:3$], which melts at 145—146° is obtained; it is hydrolysed to 3-nitro-1:4-toluidine.

Toluene-p-*sulphondiphenylamide*, $C_6H_4Me\cdot SO_2\cdot NPh_2$, crystallises from alcohol or dilute acetic acid in white needles and melts at 141°. The p-*dinitro*-derivative, $C_6H_4Me\cdot SO_2\cdot N(C_6H_4\cdot NO_2)_2$, forms pearly flakes and melts at 167—168°, but a more soluble o-*dinitro*-derivative is also formed.

Phenyl p-*toluenesulphonate*, $C_6H_4Me\cdot SO_3Ph$, forms white needles and melts at 95—96°. On nitration, it gives the *p*-nitro-ether.

Phenyl o-*nitrotoluene*-p-*sulphonate*, $NO_2 \cdot C_6H_3Me \cdot SO_3Ph$, forms white needles and melts at 59—60°.

o-*Tolyl* p-*toluenesulphonate*, $C_6H_4Me \cdot SO_3 \cdot C_6H_4Me$, forms long, white needles and melts at 54—55°. The *dinitro*-derivative,

$$C_6H_4Me \cdot SO_3 \cdot C_6H_2Me(NO_2)_2\,[Me:(NO_2)_2:OH = 1:3:5:2],$$

crystallises from alcohol and melts at 108—109°. The 6-mononitro-derivative was also produced but not hydrolysed. The m-*tolyl* ester crystallises in white needles and melts at 51°. The p-*tolyl* ester melts at 69—70°.

o-*Tolyl* o-*nitrotoluene*-p-*sulphonate*, $NO_2 \cdot C_6H_3Me \cdot SO_3 \cdot C_6H_4Me$, crystallises in white needles and melts at 68—69°. The m-*tolyl* ester melts at 63° and the p-*tolyl* ester at 95°. T. M. L.

Dimethylindenes contained in Tar. By JOHANNES BOES (*Chem. Centr.*, 1902, i, 811; from *Ber. Deut. pharm. Ges.*, **12**, 84—86).—The dimethylindenes contained in tar have been isolated from the fraction boiling at 220—230° and their constitution determined by converting them into the corresponding benzenetetracarboxylic acids, prehnitic, mellophanic, and pyromellitic acids respectively. Assuming that all the six possible isomerides are present, then from the quantity of acid obtained it may be inferred that the tar contains the largest proportion of 4 : 6- and 5 : 7-dimethylindene, a less amount of 4 : 5-, 4 : 7-, and 6 : 7-dimethylindene, and a minimum of 5 : 6-dimethylindene. E. W. W.

2 : 2′-Dinitrodiphenyl and its Derivatives. FRITZ ULLMANN (D.R.-P. 126961).—*o*-Nitroaniline and its derivatives, when diazotised and treated with cuprous chloride, either in solution or suspension, give rise to diphenyl substitution products.

2 : 2′-Dinitrodiphenyl (compare Täuber, Abstr., 1892, 480) is readily obtained from *o*-nitroaniline.

2 : 2′-*Dinitro*-4 : 4′-*ditolyl*, prepared from *m*-nitro-*p*-toluidine (m. p. 114°), crystallises from glacial acetic acid or benzene in yellowish-brown leaflets and melts at 139°.

4 : 4′-*Dichloro*-2 : 2′-*dinitrodiphenyl* and 5 : 5′-*dichloro*-2 : 2′-*dinitrodiphenyl*, obtained respectively from *p*-chloro-*o*-nitroaniline and *m*-chloro-*o*-nitroaniline, crystallise in brown needles melting at 136° and 170°. They dissolve readily in acetic acid, but only sparingly in alcohol.

2 : 2′-*Dinitrodiphenyl*-4 : 4′-*disulphonic acid*, produced from ammonium *o*-nitroaniline-*p*-sulphonate, is isolated as a brown mass; its *potassium* salt is very soluble in water, but dissolves only sparingly in boiling alcohol. G. T. M.

***s.-o-p*-Dinitrodiphenylmethane.** By KARL SCHORLEMMER (*J. pr. Chem.*, 1902, [ii], **65**, 305—307). ***o*-Nitrobenzophenone.** By ALEXANDER VON TATSCHALOFF (*ibid.*, 308—310). ***s.-o-p*-Diaminobenzophenone.** By OTTO BENÖHR (*ibid.*, 310—313).—The purification, by distillation with steam, of *o*-nitrodiphenylmethane, prepared from *o*-nitrobenzyl chloride and benzene, is unnecessary before the preparation of its derivatives by nitration or oxidation (compare Abstr., 1885, 1236, and 1895, i, 232, 233). 2 : 4′-Diaminobenzophenone yields a *hydrobromide*, $C_{13}H_{12}ON_2,2HBr$, and a *diacetyl* derivative which melts at 170°. G. Y.

s-Di-o-nitrodiphenylmethane. By Karl Schnitzspahn (*J. pr. Chem.*, 1902, [ii], **65**, 315—326).—Crude 4 : 4′-diaminodiphenylmethane is best purified by fractional precipitation from a solution of its hydrochloride. Nitration leads to 2 : 2′-dinitro-4 : 4′-diaminodiphenylmethane, which melts at 205° (compare Abstr., 1892, 618). Its *sulphate* forms white needles easily soluble in alcohol. Its hydrochloride contains $2\frac{1}{2}H_2O$. When diazotised and boiled with alcohol, it yields 2 : 2′-*dinitrodiphenylmethane*, which forms slightly yellow leaflets melting at 159°, and a small amount of needles which melt at 116°, and are converted into dinitrodiphenylmethane by heating at 100°, or by solution in alkali and precipitation by an acid.

2 : 2′-Dinitrodiphenylmethane is easily soluble in alcohol, ether, glacial acetic acid, or ethyl acetate. It is easily soluble in dilute alkalis, and is reprecipitated unchanged by acids. On boiling the alkaline solution, alkali nitrite is formed, and on acidification a brown, amorphous substance is precipitated.

Oxidation of 2 : 2′-dinitrodiphenylmethane by chromic acid in glacial acetic acid solution leads to the formation of 2 : 2′-dinitrobenzophenone. Reduction by stannous chloride yields 2 : 2′-*diaminodiphenylmethane*, which forms white needles melting at 160°. G. Y.

Di-o-nitrodiphenylmethane and Di-o-nitrobenzophenone. By W. Bertram (*J. pr. Chem.*, 1902, [ii], **65**, 327—345).—2 : 2′-Dinitro diphenylmethane (m. p. 158·5—159·5°) gives a blood-red colour with a drop of concentrated sodium hydroxide solution, and dissolves completely on dilution with water. The product obtained by boiling with alkali and addition of acid melts at 186—189°. Addition of bromine to the alkaline solution oxidises it to 2 : 2′-dinitrobenzophenone. Reduction by iron and acetic acid converts it into 2 : 2′-diaminobenzophenone and 2 : 2′-diaminodiphenylmethane.

2 : 2′-Diaminodiphenylmethane is easily soluble in alcohol, less so in ether or benzene, and only slightly so in water, from which it crystallises in leaflets. Its hydrochloride crystallises in needles.

2 : 2′-Diaminobenzophenone forms a *hydrobromide* which crystallises in white leaflets, becoming yellow on exposure to light, and a *hydrochloride* crystallising in white leaflets which rapidly become reddish. Both salts are insoluble in benzene or ether, and are decomposed by water or alcohol. With sulphuric acid, the base forms a *sulphate*, $C_{13}H_{12}ON_2,H_2SO_4$, which crystallises in short, yellow prisms, and a hydrogen *sulphate*, $C_{13}H_{12}ON_2,2H_2SO_4$, which crystallises in slightly red needles. The *picrate*, $C_{13}H_{12}ON_2,(C_6H_3O_7N_3)_2$, forms orange-coloured needles, which are easily soluble in warm water or alcohol, and decompose at 164—165°. The action of acetic anhydride on the base leads to the *diacetyl* derivative which crystallises from alcohol in yellow needles and from ethyl acetate in prisms melting at 154°, and a *substance* which melts at 164—166°. The base yields yellow crystalline diazo-salts which form red to violet dyes with resorcinol and β-naphthol.

Reduction of 2 : 2′-diaminobenzophenone with amyl alcohol and sodium yields a *base* which crystallises in glistening, white leaflets and melts at 131—133°. It forms a *hydrochloride* crystallising in white needles, and an *acetyl* derivative which crystallises in white needles and melts at 197—198°.

Methylation of 2 : 2′-diaminobenzophenone yields a *tetramethyldiaminobenzophenone* which crystallises in golden prisms, melts at 117—118°, is easily soluble in alcohol, ether, or benzene, and is volatile with steam. The *hydrochloride* crystallises in delicate needles or compact crystals. The hydrogen *sulphate*, $C_{17}H_{20}ON_2,2H_2SO_4$, is easily soluble in water and crystallises in slightly yellow needles. The *picrate* crystallises from water in light yellow leaflets, from benzene in needles, and decomposes at 160—162°. Reduction of the tetramethyl base by amyl alcohol and sodium results in the decomposition of the ketone with probable formation of dimethylaniline. G. Y.

[Phenanthrene Sulphonic Acids and Phenanthrols]. By ALFRED WERNER [with BERNH. LÖWENSTEIN, AD. WACK, TOBIAS FREY, MAX KUNZ, K. REKNER, ADOLF NEY, H. HEIL, ADOLF SCHERRER, H. SCHWABACHER, JOHANNES KUNZ, and A. GROB] (*Annalen*, 1902, **321**, 248—357. Compare Abstr., 1901, i, 696).—Sulphonation of phenanthrene, either with the ordinary concentrated or the fuming acid, shows that the phenanthrene sulphonic acids containing their sulphonic radicles in positions 2 and 3 are the chief products at 120—130°, whilst at 95—100° a good yield of phenanthrene-10-sulphonic acid is obtained. At temperatures above 140°, the amount of hydrocarbon destroyed becomes very large, and only a little of the 3-sulphonic acid is produced.

Potassium phenanthrene-3-sulphonate, $C_{14}H_9SO_3K$, crystallises in nacreous leaflets, the *barium* salt, $Ba(C_{14}H_9SO_3)_2,2\frac{1}{2}H_2O$, is a pale yellow, granular powder. The free *sulphonic acid* separates in yellow, felted needles; the *chloride* crystallises from glacial acetic acid in pale yellow needles melting at 108·5°, and the *anilide*, $C_{14}H_9\cdot SO_2\cdot NHPh$, from dilute alcohol in lustrous white needles melting at 161°. The *methyl ester*, produced by the action of dimethyl sulphate on the potassium salt, melts at 119—120°.

*Potassium phenanthrene-*10*-sulphonate* crystallises in anhydrous, hexagonal plates, and yields phenanthraquinone on treatment with chromic acid, the *barium* salt crystallises in needles with $2\frac{1}{2}H_2O$. The *sulphonic acid* separates from very concentrated solutions in lustrous white needles; the *chloride* crystallises in stellar aggregates of needles melting at 125·5°; and the *anilide*, $C_{14}H_9SO_2\cdot NHPh$, separates in prismatic crystals and melts at 165°.

Ammonium phenanthrene-2-sulphonate, obtained by boiling the crystallised ferrous salt with excess of ammonia, separates in white leaflets; it is reconverted into phenanthrene by heating with concentrated hydrochloric acid at 250°. The *potassium* salt, prepared by boiling the preceding compound with potassium hydroxide solution until all the ammonia is removed, crystallises in white leaflets. The *methyl ester*, $C_{14}H_9\cdot SO_3Me$, obtained by the action of methyl sulphate on the potassium salt, crystallises in white leaflets melting at 96—98° and having a blue fluorescence. The free sulphonic acid is not crystallisable.

3-Phenanthrol, obtained by fusing the corresponding potassium sulphonate with potassium hydroxide, melts at 122—123° and yields a *picrate* and a methyl ether melting respectively at 159° and 60—61° (compare Pschorr, Abstr., 1900, i, 233, 488).

Nitro-3-phenanthryl methyl ether, $NO_2\cdot C_{14}H_8\cdot OMe$, produced from the methyl ether by the action of nitric acid in glacial acetic acid solution, crystallises from alcohol in yellow needles and melts at 136·5—137°; on reduction with tin and hydrochloric acid, it yields *amino-3-phenanthryl methyl ether*, $NH_2\cdot C_{14}H_8\cdot OMe$, a substance crystallising in brown needles melting at 117—118° and yielding an insoluble hydrochloride which gives rise to an azo-compound on treatment with nitrite, and an alkaline solution of β-naphtholdisulphonic acid G. It was not, however, found possible to replace the amino-group by hydroxyl or chlorine.

Acetylamino-3-phenanthryl methyl ether, $OMe\cdot C_{14}H_8\cdot NHAc$, obtained by heating the amine with acetic anhydride, crystallises in white leaflets, melts at 150°, and on oxidation with chromic acid furnishes a methoxyphenanthraquinone melting at 204°, this result indicating that the amino-group is situated in position 9 or 10.

3-*Phenanthryl ethyl ether*, $C_{14}H_9\cdot OEt$, prepared by the action of ethyl iodide and sodium ethoxide on an alcoholic solution of 3-phenanthrol, separates in white crystals and melts at 46°; it may also be produced by means of diethyl sulphate. The ether is readily nitrated, yielding a *nitro*-compound crystallising in yellow needles and melting at 109—110°.

3-*Phenanthryl benzyl ether*, $C_{14}H_9\cdot O\cdot C_7H_7$, obtained by the interaction of 3-phenanthrol, benzyl chloride, and sodium ethoxide, crystallises in lustrous leaflets, melts at 91—93°, and is readily soluble in the usual organic solvents.

3-*Phenanthroxyacetic acid*, $C_{14}H_9\cdot O\cdot CH_2\cdot CO_2H$, results from the action of chloroacetic acid on an alkaline solution of 3-phenanthrol, and crystallises from ether in white, silky needles melting at 189—191°.

3-*Phenanthryl acetate*, $C_{14}H_9\cdot OAc$, produced by heating the phenol with acetic anhydride at 120—130°, crystallises from alcohol in white plates and melts at 115—116°.

3-*Phenanthryl benzoate*, $C_{14}H_9\cdot OBz$, which is prepared by adding benzoyl chloride to a pyridine solution of phenanthrol, crystallises from dilute alcohol in needles melting at 119°.

3-*Phenanthryl benzenesulphonate*, $C_{14}H_9\cdot O\cdot SO_2Ph$, obtained by the Schotten-Baumann reaction, crystallises from methyl alcohol in stellar aggregates of prisms melting at 105—107°.

Tri-3-phenanthryl phosphate, $PO(O\cdot C_{14}H_9)_3$, produced by treating a strongly alkaline solution of 3-phenanthrol with phosphorus oxychloride, crystallises from toluene in small leaflets melting at 180—182°.

Sodium 3-phenanthrolazobenzenesulphonate,

$$OH\cdot C_{14}H_8\cdot N_2\cdot C_6H_4\cdot SO_3Na,H_2O,$$

is precipitated by adding hydrochloric acid to an alkaline solution of 3-phenanthrol and diazobenzenesulphonic acid; it crystallises from dilute alcohol in lustrous red needles and dyes silk with a cherry-red colour.

Amino-3-phenanthrol results from the reduction of the preceding azo-compound with tin and hydrochloric acid, and crystallises from dilute alcohol in lustrous white needles melting at 159—161°. On treatment with nitrous acid, it yields a yellow compound which becomes resinous on warming. *Amino-3-phenanthrol hydrochloride* is most readily obtained by passing hydrogen chloride into an ethereal solution of the base; in hot aqueous solutions, oxidation occurs with the formation of a blue, soluble substance. *Diacetylamino-3-phenanthryl acetate*, the ultimate product of the action of acetic anhydride on the preceding amine, crystallises in sparingly soluble needles melting at 169—170°.

10-Phenanthrol (phenanthrone), produced by subjecting potassium phenanthrene-10-sulphonate to fusion with potash at 280—290°, crystallises from petroleum in lustrous pink needles melting at 152° (compare Abstr., 1883, 666; 1884, 81); the *picrate* crystallises from absolute alcohol in red needles melting at 183°.

10-Phenanthryl acetate forms needles melting at 77°; 10-*phenanthryl propionate*, obtained by the interaction of 10-phenanthrol and propionic anhydride at 180°, crystallises from glacial acetic acid in white needles melting at 95°. These compounds show that 10-phenanthrol (phenanthrone) is really a phenol and not a ketodihydrophenanthrene. 10-*Phenanthryl benzoate* and 10-*phenanthryl benzenesulphonate*, $C_{14}H_9{\cdot}O{\cdot}SO_2Ph$, crystallise from dilute alcohol in white needles melting respectively at 96·7° and 88·5°; the former is obtained by mixing the phenol with benzoyl chloride in pyridine solution, the latter is produced by the Schotten-Baumann reaction.

Benzeneazo-10-*phenanthrol*, $N_2Ph{\cdot}C_{14}H_8{\cdot}OH$, prepared by coupling benzenediazonium chloride and 10-phenanthrol in alkaline solution, crystallises from glacial acetic acid in deep red leaflets with a green reflex; it melts at 162—163°, and is identical with phenanthraquinone hydrazone (Zincke, *Ber.*, 1883, **16**, 1564).

2-*Phenanthrol*, resulting from the fusion with potash of the ammonium or potassium salt of phenanthrene-2-sulphonic acid, crystallises from petroleum in lustrous, white leaflets and melts at 169°.

2-*Phenanthryl methyl ether*, $C_{14}H_9{\cdot}OMe$, produced either by adding methyl iodide to sodium 2-phenanthroxide in absolute alcohol or by mixing an alkaline solution of the phenol with methyl sulphate, crystallises from glacial acetic acid in white leaflets melting at 100—101°; its *nitro*-derivative, obtained by nitration in glacial acetic acid, crystallises from this solvent in greenish-yellow leaflets melting at 190—191°.

2-*Phenanthryl acetate* crystallises from the ordinary organic solvents in white needles and melts at 142—143°.

2-*Phenanthryl benzoate*, produced by mixing its generators in pyridine solution, is obtained in white leaflets and melts at 139—140°.

2-*Phenanthrolazobenzenesulphonic acid*, $SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_8{\cdot}OH$, prepared by coupling the phenol with diazobenzenesulphonic acid in alkaline solution, is an amorphous, red substance dyeing yellow shades on silk.

A comparison of the properties of the preceding phenanthrols with those of the hydroxyphenanthrenes obtained by earlier investigators, shows that Siemienski and also Rehs (Abstr., 1878, 76) were dealing with mixtures of the three isomerides; the phenanthrol described as melting at 112° is not a simple substance.

3-Phenanthrylamine, produced by heating the corresponding phenol with ammonia and ammonium chloride, exists in two modifications melting at 143° and 87·5° (compare Kunz, Abstr., 1901, i, 696); the modification of higher melting point changes into the more fusible variety on keeping for four months, and appears to be a labile polymeride. Both varieties yield the same acetyl derivative melting at 200—201°.

Benzoyl-10-*phenanthrylamine* crystallises from xylene in white, silky needles melting at 211°; the *phenylcarbamide* is a white, amorphous substance not melting below 290°; the *urethane* derivative, $C_{14}H_9{\cdot}NH{\cdot}CO_2Et$, crystallises in silky needles and melts at 123°.

2-Phenanthrylamine yields *benzoyl* and *urethane* derivatives crystallising in white needles and melting at 216·5° and 125°; the *phenylcarbamide* is amorphous and decomposes at 276°.

Phenyl-2-*phenanthrylamine*, produced by heating the corresponding phenanthrol with aniline and calcium chloride, separates from light petroleum in hard, greenish crystals.

Potassium 3-phenanthrenesulphonate, when heated with anhydrous potassium ferrocyanide, yields 3-*phenanthryl cyanide* crystallising from alcohol in white needles melting at 102°; the product, on hydrolysis with potassium hydroxide in methyl alcohol, gives rise first to 3-*phenanthramide*, $C_{14}H_9{\cdot}CO{\cdot}NH_2$, and finally, after 55 hours, to 3-phenanthroic acid; the amide and acid crystallise in lustrous flakes melting at 227—228° and 269° respectively. This acid is identical with the substance obtained by Anschütz and by Japp.

10-*Phenanthryl cyanide*, produced by heating a mixture of the corresponding sulphonate and excess of potassium ferrocyanide, crystallises from alcohol in slender needles melting at 103°, and readily yields its amide and carboxylic acid on hydrolysis with potassium hydroxide dissolved in methyl alcohol. 10-*Phenanthramide* separates from water in white crystals melting at 226°; 10-phenanthroic acid crystallises in yellowish-white needles melting at 250°, and is identical with Japp's β-phenanthrenecarboxylic acid (Trans., 1880, **37**, 84). 2-*Phenanthryl cyanide*, $C_{14}H_9{\cdot}CN$, crystallises from a mixture of benzene and petroleum and melts at 105°. 2-*Phenanthroic acid*, $C_{14}H_9{\cdot}CO_2H$, obtained by alkaline hydrolysis in methyl alcohol solution, crystallises from glacial acetic acid in white needles melting at 254°.

The dibromophenanthrene, prepared from 10-bromophenanthrene, when quite pure, crystallises in needles, sinters at 100°, and melts at 112—113°. Dinitrophenanthraquinone, formerly obtained by Anschütz (*Ber.*, 1876, **9**, 1404) is readily produced by the use of fuming nitric acid, and when crystallised from glacial acetic acid melts at 301—303°.

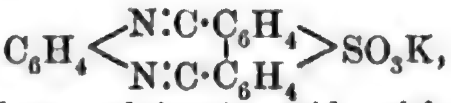
2-*Nitrophenanthraquinone* results from the action of the concentrated acid of sp. gr. 1·4.

3-*Nitrophenanthraquinone*, prepared by the action of fuming nitric acid on 10-bromophenanthrene, crystallises in orange-coloured needles and melts at 275°. On reduction with tin and hydrochloric acid, these nitroanthraquinones yield the corresponding aminophenanthraquinones; 3-*aminophenanthraquinone* crystallises from alcohol in brownish-red needles and melts at 254°; these amines are readily diazotised, and give rise to the corresponding hydroxyphenanthraquinones.

Potassium 3-phenanthraquinonesulphonate, $C_{14}H_7O_2{\cdot}SO_3K$, produced by oxidising the corresponding phenanthrenesulphonate with chromic anhydride in glacial acetic acid, crystallises from dilute alcohol in lustrous, orange-yellow, felted needles, and is very soluble in water. The *barium* salt, $(C_{14}H_7O_2{\cdot}SO_3)_2Ba,2\frac{1}{2}H_2O$, is an orange-red precipitate sparingly soluble in water.

A compound giving the reactions of an oxime is obtained by condensing the sulphonate with hydroxylamine, but was not isolated in a state of purity. When treated with a 50 per cent. solution of potassium hydroxide, the phenanthraquinonesulphonate decomposes, yielding diphenylene ketone and 3-phenanthrol; this result is due to simultaneous oxidation and reduction. The tendency to revert to the parent hydrocarbon is also exhibited by the sulphonate on heating under pressure with concentrated hydrochloric acid. In this case, simultaneous reduction and hydrolysis result in the formation of phenanthrene. Fusion of the quinonesulphonate with potash leads to the production of 3-phenanthrol.

Potassium diphenylenequinoxalinesulphonate,



$$C_6H_4{<}\begin{matrix}N{:}C{\cdot}C_6H_4\\ \vert\\ N{:}C{\cdot}C_6H_4\end{matrix}{>}SO_3K,$$

results from the condensation of the quinonesulphonic acid with *o*-phenylenediamine, and separates from water in an amorphous condition.

Methyl 3-phenanthraquinonesulphonate, produced by oxidising the corresponding alkyl phenanthrenesulphonate, is an orange-yellow, crystalline substance melting at 235°. 3-*Phenanthraquinone cyanide*, $C_{14}H_7O_2{\cdot}CN$, resulting from the oxidation of 3-phenanthryl cyanide, crystallises from glacial acetic acid in orange-coloured leaflets melting at 282—283°; the corresponding *amide* is produced by oxidising 3-phenanthramide, and crystallises in orange-red needles, melting at 289—290°. 3-Phenanthraquinonecarboxylic acid, prepared by oxidising 3-phenanthroic acid, separates in reddish-yellow crystals and melts at 310°; it has already been obtained by Schultz (*Annalen*, 1879, **196**, 14). 2-*Phenanthraquinone cyanide*, $C_{14}H_7O_2{\cdot}CN$, produced from 2-phenanthryl cyanide, crystallises from glacial acetic acid in reddish-yellow leaflets and melts at 290°. 2-*Phenanthraquinonecarboxylic acid*, $C_{14}H_7O_2{\cdot}CO_2H$, prepared by oxidising 2-phenanthroic acid, crystallises in reddish-yellow needles and melts above 300°. G. T. M.

o-Chloro-p-nitroaniline. By PAUL COHN (*Chem. Centr.*, 1902, i, 752; from *Mitt. Technol. Gewerb-Mus. Wien* [ii], 11, 205—213. Compare Abstr., 1901, i, 407).—*o-Chloro-p-nitroaniline*, prepared from *p*-nitroaniline by Cassella & Co.'s method (*Patentbl.*, **21**, 523), crystallises from water in slender, yellow needles, melts at 105°, is slightly soluble in cold water, completely so in a large volume of hot water, and readily so in hot alcohol or ether, but insoluble in light petroleum.

The *hydrochloride* crystallises from solutions strongly acidified with hydrochloric acid in four-sided plates, and is decomposed by water. The sulphate, oxalate, and picrate are very unstable. The *acetyl* derivative, $C_8H_7O_3N_2Cl$, crystallises from alcohol in faintly brownish-yellow crystals and melts at 138—139°. The *benzoyl* derivative, $C_{13}H_9O_3N_2Cl$, crystallises in pale yellow needles and melts at 161°. The azo-derivatives of chloro-*p*-nitroaniline have a bluer tinge than those of *p*-nitroaniline itself, and are not so readily attacked by acids or by light. Chloro-*p*-nitroaniline may be converted into 3 : 4-dichloro-1-nitrobenzene by Sandmeyer's reaction and when the diazo-compound is boiled with water it yields 2-chloro-4-nitrophenol. The diazo-compound combines with β-naphtholdisulphonic acid-G., in sodium carbonate solution to form the sodium salt of the *compound*

$$NO_2\cdot C_6H_3Cl\cdot N{:}N\cdot C_{10}H_4(SO_3H)_2\cdot OH,$$

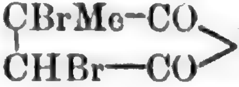
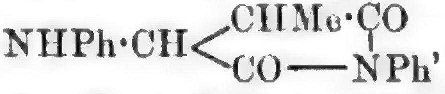
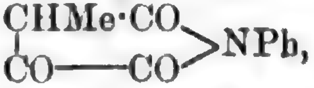
which separates as a scarlet precipitate; it dissolves on warming and on cooling crystallises in lustrous orange-red needles. The free *acid* crystallises in scarlet-red needles which have a silky lustre.

*Chloro-*p*-phenylenediamine*, obtained by reducing *o*-chloro-*p*-nitroaniline with tin and hydrochloric acid, crystallises from benzene or light petroleum in white needles and melts at 63—64°; the *hydrochloride* crystallises in colourless needles. The sulphate, nitrate, oxalate, and picrate were also prepared. The *diacetyl* derivative crystallises in white needles, melts at 197°, and is readily soluble in alcohol but only very slightly so in benzene. The *dibenzoyl* derivative crystallises from chloroform in white needles and melts at 228°. Chloro-*p*-phenylenediamine, when warmed with hydrogen sulphide and ferric chloride, yields a violet-red chlorothiazine; with aniline and potassium dichromate, it forms a greenish-blue chloroindamine, and by oxidation with phenol in alkaline solution the corresponding chloroindophenol is obtained. By the action of potassium dichromate and sulphuric acid, chloro-*p*-phenylenediamine is converted into monochloroquinone, and with concentrated hydrochloric acid and bleaching powder it yields *monochloroquinone dichlorodi-imide*, $C_6H_3Cl(NCl)_2$, which crystallises from dilute alcohol in brownish-yellow needles, has a disagreeable odour resembling that of quinone, and melts at 83—84°. This compound reacts with acetic acid and resorcinol to form a dark violet dye.

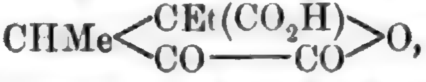
E. W. W

Pentanitro-1-nitromethylaminobenzene and Tetra- and Pentanitrophenol. By J. J. Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 4, 437—442).—By the action of concentrated nitric acid on *m*-nitromethylaniline and on 3 : 5-dinitromethylaniline, 2 : 3 : 4 : 6-tetranitro-1-nitromethylaminobenzene, and *pentanitro-1-nitromethylaminobenzene*, $C_6(NO_2)_5\cdot NMe\cdot NO_2$, have respectively been obtained. The former has previously been prepared by van Romburgh (Abstr. 1889, i, 1154) from 2 : 4 : 5-trinitrodimethylaniline; the latter is a yellow, crystalline substance melting at 132°, and exploding at a higher temperature. When nitrated with a cold mixture of nitric and sulphuric acids, *m*-nitrophenol yields 2 : 3 : 4 : 6-*tetranitrophenol*, melting at 140°, and 3 : 5-dinitrophenol yields *pentanitrophenol*, which melts at 190°. If hot nitric acid is employed as the nitrating agent, 2 : 4 : 6-

trinitroresorcinol and trinitrophloroglucinol are respectively formed, as under these conditions a nitro-group which is flanked by two other nitro-groups is replaced by hydroxyl. Such a nitro-group can similarly be readily replaced by a methoxyl, ethoxyl, amino-, or phenylamino-group. K. J. P. O.

Anilinocitraconanil and its Derivatives. By FRITZ FICHTER and ERNST PREISWERK (*Ber.*, 1902, 35, 1626—1630).—Citraconanil forms with bromine an additive *product*,  $\begin{array}{l}\text{CBrMe-CO}\\ \text{CHBr—CO}\end{array}\!>\!\text{NPh}$, which crystallises in thick plates melting at 126—127°; by treatment with aniline in ethereal solution, it is converted into bromocitraconanil (m. p. 144·5—145·5°), but when heated with excess of aniline, anilinocitraconanil (m. p. 157°) is obtained. On reduction of the last-mentioned substance with aluminium amalgam, two stereoisomeric *a-anilinomethylsuccinanils*,  $\text{NHPh}\cdot\text{CH}\!<\!\begin{array}{l}\text{CHMe}\cdot\text{CO}\\ \text{CO——NPh}\end{array}$, are formed; one crystallises in white needles melting at 186·5—187°, the other in aggregates of needles melting at 134°. On hydrolysing anilinocitraconanil with sulphuric acid, *methyloxalacetanil*,  $\begin{array}{l}\text{CHMe}\cdot\text{CO}\\ \text{CO——CO}\end{array}\!>\!\text{NPh}$, is obtained as colourless needles decomposing at 196°; it forms a yellow solution in water or alcohol which gives a dark brown coloration with ferric chloride, and its salts are yellow in colour and yield yellow solutions; the enolic form of this compound would thus appear to have a yellow colour. The *phenylhydrazone* crystallises in yellow, flattened needles melting at 183—184°. *Bromomethyloxalacetanil* forms pale yellow needles melting at 134°.

By prolonged treatment of anilinocitraconanil with concentrated sulphuric acid, *a-keto-β-methylhexolactone-γ-carboxylic acid*,



$$\text{CHMe}\!<\!\begin{array}{l}\text{CEt}(\text{CO}_2\text{H})\\ \text{CO——CO}\end{array}\!>\!\text{O},$$

is obtained, probably being produced by condensation of the propionylformic acid first formed; it forms crystals melting at 128° and gives a violet coloration with ferric chloride. K. J. P. O.

Methylation of 6-Nitro-*o*-toluidine. By ALEXANDER VON TATSCHALOFF (*J. pr. Chem.*, 1902, [ii], 65, 239—242).—The *hydrobromide* of 6-nitro-*o*-toluidine crystallises in clusters of yellowish leaflets or long, thin needles and is decomposed when treated with water. The *hydriodide* crystallises in rhombohedra or flat prisms. The hydrobromide, when heated with methyl alcohol for 6—10 hours at 100—110°, yields a mixture of 6-nitro-*o*-dimethyltoluidine and its *hydrobromide*; the base boils at 191—192° under 9·5—10 cm. pressure and solidifies in the cold to a mass of transparent golden crystals melting at 25—25·5°; the hydrobromide crystallises in bright greyish-brown leaflets. R. H. P.

Methylation of 5-Nitro-*m*-toluidine. By AD. HAIBACH (*J. pr. Chem.*, 1902, [ii], 65, 242—246. Compare preceding abstract).—The *hydrobromide* of 5-nitro-*m*-toluidine crystallises in thin leaflets.

5-*Nitro*-m-*dimethyltoluidine* crystallises from ether in dark red, flat, rhombic pyramids and melts at 48—50°. 5-*Nitro*-m-*tolyltrimethylammonium bromide* crystallises, with $2H_2O$, in large, rhombic prisms, and, when treated with moist silver oxide, yields trimethylamine and *s*-nitrocresol. R. H. P.

Methylation of 2-Nitro-*p*-toluidine. By AD. HAIBACH (*J. pr. Chem.*, 1902, [ii], **65**, 246—248. Compare preceding abstracts).—The *hydrobromide* of 2-nitro-*p*-toluidine crystallises in large laminæ. 2-*Nitro*-p-*dimethyltoluidine* was obtained as a reddish, crystalline mass melting at 35°, and 2-*nitro*-p-*tolyltrimethylammonium bromide* crystallises, with $\frac{1}{2}H_2O$, in colourless, rhombic prisms or pyramids. R. H. P.

Methylation of 4-Nitro-*o*-toluidine. By O. STADEN (*J. pr. Chem.*, 1902, [ii], **65**, 249—252. Compare preceding abstracts).—The *hydrobromide* of 4-nitro-*o*-toluidine was obtained in the form of small, lustrous, pale red crystals, 4-*nitro*-o-*dimethyltoluidine* in golden leaflets or rods melting at 14°, and 4-*nitro*-o-*tolyltrimethylammonium bromide* in small, colourless, tabular crystals. R. H. P.

Formation of Quaternary Aromatic Bases. By S. SCHLIOM (*J. pr. Chem.*, 1902, [ii], **65**, 252—257. Compare preceding abstracts).—Comparative experiments show that quaternary aromatic bases are more readily formed by compounds with a side chain in the meta- or para-position to the amino-group than by those with a side chain in the ortho-position. R. H. P.

Molecular Rearrangement of Unsymmetrical Acylthiocarbamides and Acyl-ψ-thiocarbamides into the Isomeric Symmetrical Derivatives. By HENRY L. WHEELER (*Amer. Chem. J.*, 1902, **27**, 270—280).—When phenyl-ψ-methylthiocarbamide, $NH_2\cdot C(SMe):NPh$, dissolved in dry ether, is treated at 0° with acetyl chloride, it is converted partly into an acetyl derivative and partly into the hydrochloride. The former crystallises from ether in colourless prisms melting at 85—86° and is decomposed in the cold by alkalis with the formation of methyl thiocyanate and acetanilide and has therefore the constitution $NH:C(SMe)\cdot NPh\cdot COMe$. It combines with hydrogen iodide to form a hydriodide, insoluble in ether, crystallising from hot alcohol in the form of colourless four- and six-sided plates and melting at 152°. The latter is also formed by the addition of methyl iodide to the labile acetylphenylthiocarbamide obtained by Hugershoff (Abstr., 1900, i, 156), which must therefore be represented by the formula $NH_2\cdot CS\cdot NPhAc$ instead of $NHPh\cdot CS\cdot NHAc$, as proposed by the latter author. The transformation of these unsymmetrical thiocarbamides into their symmetrical isomerides may be represented as taking place in one of the two following ways: $NH_2\cdot CS\cdot NPhAc \rightarrow NHAc\cdot CS:NHPh$ or $NH:C(SH)\cdot NPhAc \rightarrow NHAc\cdot C(SH):NPh$.
T. A. H.

Removal of Sulphur from Aryldithiocarbamates. By GUSTAVE HELLER and WILHELM BAUER (*J. pr. Chem.*, 1902, [ii], **65**, 365—386).—Monoarylthiocarbamides are obtained by the action of lead carbonate (1 mol.) on the corresponding ammonium aryldithiocarbamates; by the action of lead carbonate (2 mols.) in the presence of alkali (1 mol.), arylcyanamides are formed.

The following new compounds are described:

p-*Tolylcyanamide* crystallises in prisms, melts at 69°, and is easily soluble in alcohol, ether, chloroform, or benzene. Its *silver* derivative, $C_8H_7N_2Ag$, crystallises in leaflets; the *platinichloride* forms orange-red prisms which decompose at about 155°. The *benzoyl* derivative melts at 126°. *p*-Tolylcyanamide and glycine condense to form glycolmono-*p*-tolylguanidine, $C_{10}H_{13}O_2N_3$, which is soluble in dilute hydrochloric acid, becomes brown at 240°, and melts with evolution of gas at 262°. When heated in benzene solution, *p*-tolylcyanamide polymerises to *tri*-p-*tolyliso-melamine*, which crystallises with benzene in needles, $C_{24}H_{24}N_6,C_6H_6$, melting at 183°. It is easily soluble in ether, alcohol, or hydrochloric acid. The crystals lose C_6H_6 at 135—140°. It yields a *triacetyl* derivative which forms colourless crystals, becoming slightly yellow at 205° and melting with decomposition at 236°.

m-*Tolylcyanamide* forms crystals which melt at the ordinary temperature. Its *benzoyl* derivative melts at 69°.

β-Naphthylcyanamide crystallises in colourless leaflets, melts at 102° and is easily soluble in alcohol, ether, or chloroform.

p-Ethoxyphenylthiocarbamide is found to melt at 172° and *p*-ethoxyphenylcyanamide at 87° (compare Abstr., 1885, 148). When recrystallised from benzene, the cyanamide yields a substance, probably a *polymeride*, melting at 170°.

When boiled with water, ammonium phenyldithiocarbazinate yields diphenylthiosemicarbazide (m. p. 176°), hydrogen sulphide, ammonia, phenylhydrazine, and a yellow substance which melts at 80—85°.

Phenyl-o-*tolylguanidine* formed from *o*-tolylcyanamide and aniline hydrochloride, or from phenylcyanamide and *o*-toluidine hydrochloride, melts at 123—125°. o-p-*Ditolylguanidine* melts at 120—121° *Phenyl*-p-*tolylguanidine* melts at 120—122°. G. Y.

Acetyl Compounds of Benzenoid and Naphthalenoid Aminosulphonic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 129000).—The neutral salts of the aromatic aminosulphonic acids, when suspended or dissolved in water at the ordinary temperature or at 50°, can be readily acetylated by the addition of acetic anhydride. The acetyl derivatives of sulphanilic, metanilic, *o*- and *p*-toluidinesulphonic, and *o*, *m*-, and *p*-aminobenzoic acids have been obtained in this way and the reaction is equally applicable to the sulphonic acids of *α*- and *β*-naphthylamine. The salts of *m*- and *p*-phenylenediaminesulphonic and *m*-tolylenediaminesulphonic acids yield the *mono*- or *di-acetyl* derivatives, according to the amount of acetic anhydride employed. G. T. M.

Preparation of Oxyamidines. By HEINRICH LEY (*Ber.*, 1902, **35**, 1451—1453).—Oxyamidines can be advantageously prepared by the action of *β*-substituted hydroxylamines on imino-ethers. From phenylhydroxylamine and methyl*iso*formanilide, OMe·CH:NPh, Bamberger and Tschirner's diphenyloxyformamidine (this vol., i, 276) was obtained, whilst *p*-tolylhydroxylamine gave 1-*phenyl*-3-p-*tolyloxyform-*

amidine, of which the *copper* salt only was isolated; this crystallises from toluene and melts at 248°. T. M. L.

Structure of the Substances obtained by the Addition of Organic Oxygen Compounds and Aluminium Haloids. By Elmer P. Kohler (*Amer. Chem. J.*, 1902, **27**, 241—257).

—When an aluminium haloid is mixed with an oxygenated carbon compound, dissolved in a suitable solvent, for example, carbon disulphide, an additive product is formed containing 1 mol. of the aluminium salt with 2 mols. of the substance, if the latter contains one atom of oxygen, or with 1 mol. if it contains two oxygen atoms: thus aluminium bromide combines with anthraquinone to form the derivative $Al_2Br_6,C_{14}H_8O_2$, and with phenyl ether to produce the compound $Al_2Br_6,2(C_6H_5)_2O$. Similar additive products of anisole, terephthalyl chloride, methylene, phenylene ether, acetophenone, acetylmesitylene and its chloro- and dichloro-derivatives, dibenzylideneacetone, xanthone, acetylacetone, and chloroacetyl chloride have been isolated. These substances usually crystallise well, dissolve in carbon disulphide, and decompose when heated. The observations of the author are not in accord with the formulæ proposed by Gustavson (Abstr., 1888, 575) and by Kronberg (Abstr., 1900, i, 502) for compounds of this type, and he proposes to represent them as containing quadrivalent oxygen thus:

$$OR_2Cl\cdot AlCl_2\cdot AlCl_2\cdot OR_2Cl.$$

T. A. H.

Sitosterol. By E. Ritter (*Zeit. physiol. Chem.*, 1902, **34**, 461—480. Compare Burian, Abstr., 1898, i, 72).

—Sitosterol, after six crystallisations from alcohol, melts at 136·5°. In ethereal solution, it gives $[\alpha]_D$ $-26·40°$ and in chloroform solution $-33·91°$. Analyses agree best with one or other of the formulæ $C_{26}H_{43}\cdot OH,H_2O$, $C_{27}H_{45}\cdot OH,H_2O$.

The alcoholic mother liquors yield a second crystalline modification of sitosterol in the form of flat needles.

The following esters have been prepared, namely: Benzoate melting at 145·5; *cinnamate* melting at 158° and exhibiting strong fluorescence; *palmitate* from sitosterol and palmitic acid, glistening flakes melting at 90°; *stearate* melting at 89—90° to a turbid liquid which clarifies at 118—119°; *oleate*, colourless needles melting at 35·5°. Boiling alcoholic potash is practically without action on sitosterol.

J. J. S.

Bufonin and Bufotalin, the Active Components of the Secretions of the Skin Glands of the Toad. By Edwin S. Faust (*Chem. Centr.*, 1902, i, 891—892; from *Arch. exp. Path. Pharm.*, **47**, 278—310).

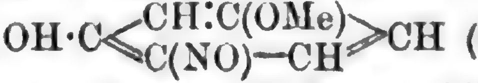
—*Bufonin*, $(C_{17}H_{26}\cdot OH)_2$, obtained by extracting the skins of toads with 96 per cent. alcohol, crystallises from alcohol in slender needles or thicker prisms, melts at 152°, and is readily soluble in chloroform, benzene, or hot alcohol. With chloroform and with acetic anhydride and concentrated sulphuric acid, it gives reactions similar to those of cholesterol, but it does not give the cholesterol reaction with hydrochloric acid and ferric chloride, and is not attacked by boiling with alcoholic sodium hydroxide solution. *Bufonin chloride*, prepared by the action of phosphorus pentachloride on bufonin, crystallises from hot alcohol in needles grouped together in feathery aggregates and melts at 103°. When the chloride is reduced with sodium ethoxide, a hydrocarbon (analogous to cholestene ?) is obtained which forms an additive compound with bromine.

The alcoholic extract of the skin also contains an acid *bufotalin*, $C_{34}H_{46}O_{10}$ which is probably an oxidation product of bufonin; it is very soluble in chloroform, alcohol, glacial acetic acid, acetone, or alkalis. Bufotalin is precipitated by tannin, or by phosphotungstic or phosphomolybdic acid.

When bufotalin is oxidised by chromic mixture, a product is obtained of which a portion is soluble in ammonia; on acidification, the ammoniacal solution gives a white, flocculent precipitate the physiological properties of which resemble those of bufotalin. Bufotalin is the active component of the secretion of the skin of the toad, and when injected subcutaneously, it has a physiological action similar to that of digitalin, diminishing the frequency of the pulse, but increasing its volume and the pressure of the blood in warm-blooded animals. When applied subcutaneously, it affects the intestines and respiratory organs, eventually causing death, but it has no action on the nervous system. Administration *per os* only causes local irritation, and very large doses are required to be fatal. Bufonin is less soluble than bufotalin and has consequently a weaker physiological action.

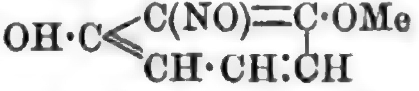
A cholesterol derivative possessing similar physiological properties has also been prepared. E. W. W.

Action of Nitrous Acid on Resorcinol Monomethyl Ether. By Ferdinand Henrich and Otto Rhodius (*Ber.*, 1902, **35**, 1475—1486. Compare Abstr., 1896, i, 476, and 1900, i, 163).—The monomethyl ether of resorcinol (1 mol.) dissolved in a mixture of alcohol and acetic acid, was treated with a concentrated solution of sodium nitrite (1 mol.); the product, when dry, was extracted with cold benzene; the soluble material consists of (i) a small quantity of a very soluble *nitroso*-derivative,



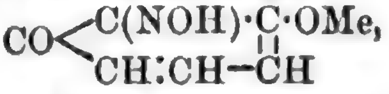
$\mathrm{OH\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{CH{:}C(OMe)}}{\mathrm{C(NO){-}CH}}{>}\mathrm{CH}$

(?), which forms brownish crystal aggregates melting at 138°; and (ii) a much larger quantity of a less soluble isomeric *nitroso*-derivative,



$\mathrm{OH\cdot C}{<}\genfrac{}{}{0pt}{}{\mathrm{C(NO){=}C\cdot OMe}}{\mathrm{CH\cdot CH{:}CH}}$

or



$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{C(NOH)\cdot C\cdot OMe,}}{\mathrm{CH{:}CH{-}CH}}$

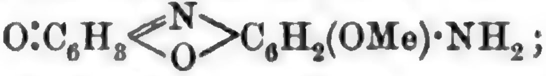
which exists in two modifications; the one forms green crystals, which become suddenly yellow at 128—130° and melt at 154°, and is obtained when the compound is crystallised from benzene; the other form is obtained from alcoholic solutions of the nitroso-derivative, and crystallises in brownish-yellow needles melting at 154°. Both forms have mol. weights corresponding with the simple formula. The view is expressed that one form corresponds with an *o*-quinoneoxime, and the other to an *o*-nitrosophenol. The *potassium* salt, $OMe\cdot C_6H_3(NO)\cdot OK$, is obtained by mixing alcoholic solutions of potassium hydroxide and the nitroso-derivative.

On reduction with stannous chloride and hydrochloric acid, both forms yield the *hydrochloride* of 2-amino-3-methoxyphenol,

$$OMe\cdot C_6H_3(OH)\cdot NH_2,HCl,$$

which forms crystals melting at 214°; the base is very readily oxidised; the *picrate* forms yellowish-green crystals; the *triacetyl* derivative, $OMe\cdot C_6H_3(OAc)\cdot NAc_2$, obtained when the hydrochloride is heated with acetic anhydride at 140°, crystallises in small cubes melting at 92°. When the last-mentioned substance is heated at 200—240°, *2-methyl-4-methoxybenzoxazole*, $OMe\cdot C_6H_4{<}\substack{N\\O}{>}CMe$, distils over, and crystallises in large, white needles melting at 57°. On benzoylating the hydrochloride of the base by the Schotten-Baumann method, a *monobenzoyl* derivative is obtained melting at 163°; when distilled, *4-methoxy-3-phenylbenzoxazole*, $OMe\cdot C_6H_4{<}\substack{N\\O}{>}CPh$, is formed, and crystallises in yellowish needles melting at 65—66°.

An alkaline solution of 2-amino-3-methoxyphenol is rapidly oxidised by the air, with the production of a *phenoxazine*,



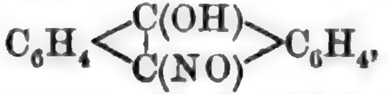
$$O{:}C_6H_3{<}\substack{N\\O}{>}C_6H_2(OMe)\cdot NH_2;$$

it crystallises in dark-red crystalline aggregates, which darken at 260—270°, melt and decompose at 300—302°, and dissolve in sulphuric acid with a violet coloration, becoming red on adding water; the *monoacetyl* derivative crystallises in brick-red needles. On reduction of the phenoxazine with zinc dust and acetic acid in the presence of acetic anhydride, a *substance*, $C_{13}H_9O_3N_2(OAc)_3$, was obtained as colourless crystals.

p-*Nitroso*-m-*methoxyphenol*, $OMe\cdot C_6H_3(NO)\cdot OH$, is left undissolved on extracting with cold benzene the product of the action of nitrous acid on resorcinol monomethyl ether; it crystallises in yellow leaflets, which begin to darken and decompose at 160—170°; on reduction, p-*amino*-m-*methoxyphenol hydrochloride* is obtained, crystallising in greyish-blue crystals. Oxidation of the latter produces methoxyquinone (m. p. 140°). K. J. P. O.

*s-o-p-***Dihydroxydiphenylmethane.** By VICTOR WAGNER (*J. pr. Chem.*, 1902, [ii], **65**, 313—315).—*2 : 4′-Dihydroxydiphenylmethane*, obtained from 2 : 4′-diaminodiphenylmethane, crystallises from alcohol in delicate needles or straw-yellow, rhombic prisms, melts at 117—118°, and is slightly soluble in water, easily in alcohol or ether. It yields a *dibenzoyl* derivative which forms silky needles melting at 108°, a *diacetyl* derivative which crystallises in delicate, glistening needles melting at 70°, a *diethyl* ether, which forms white needles melting at 60°, and a *dimethyl* ether which separates from methyl alcohol in colourless crystals which melt at 26°. G. Y.

o-**Nitroanthracene [Nitrosoanthranol].** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127399).—9-Nitrosoanthranol,



$$C_6H_4{<}\substack{C(OH)\\|\\C(NO)}{>}C_6H_4,$$

prepared by adding 60 per cent. nitric acid to a suspension of anthracene in glacial acetic acid, is precipitated from the clear yellow solution thus obtained in the form of anthracene nitrochloride by the addition of concentrated hydrochloric acid; this intermediate product separates from benzene or toluene in white needles melting at 163°, and is converted into nitrosoanthranol by treatment with a solution of ammonia, sodium hydroxide, or the corresponding carbonate.

The yellow solution obtained by the action of nitric acid when poured into water and treated with alkaline solutions also yields nitrosoanthranol, and this substance is also obtained by adding concentrated sulphuric acid to the product of nitration dissolved either in glacial acetic acid or in nitrobenzene. G. T. M.

Molecular Fission produced by Bromine. By R. Fosse (*Compt. rend.*, 1902, **134**, 904—906. Compare Abstr., 1901, 322, 384, 604, 643, and this vol., i, 51, 171, 304).—The *eso*anhydride of 2 : 2′ : 2″-trihydroxy-1 : 1′ : 1″-trinaphthylmethane, when treated with bromine in bromoform or glacial acetic acid, undergoes disruption, a mol. of the substance yielding 1 mol. of 1-bromo-β-naphthol and 1 mol. of dinaphthaxanthonium bromide. The original substance having been formed by the condensation of 2-hydroxy-1-naphthaldehyde and β-naphthol, this decomposition affords an indirect method of substituting bromine for the aldehydic complex. The fact that 1-bromo-β-naphthol is the product of the fission is additional evidence in favour of the constitution assigned to 2-hydroxy-1-naphthaldehyde. G. T. M.

Constitution of Chlorohydrins. By Marc Tiffeneau (*Compt., rend.*, 1902, **134**, 774—775).—The action of hypochlorous acid on β-phenylmethylethylene (β-allylbenzene), $CPhMe{:}CH_2$, yields a chlorohydrin which has a sp. gr. 1·220 at 0°, boils at 130—132° under 16 mm. pressure and is identical with the chlorohydrin,

$$OH{\cdot}CPhMe{\cdot}CH_2Cl,$$

obtained by the action of chloroacetone on magnesium phenyl bromide. The action of chloroacetone on magnesium methyl iodide yields the chlorohydrin, $OH{\cdot}CMe_2{\cdot}CH_2Cl$, and its action on magnesium ethyl bromide yields the chlorohydrin, $OH{\cdot}CMeEt{\cdot}CH_2Cl$, which boils at 149—151°, and has a sp. gr. 1·053 at 0°. These results are regarded as supporting Krassusky's conclusion (Abstr., 1901, i, 246) that when hypochlorous acid combines with ethylenic hydrocarbons the hydroxyl group always attaches itself to the carbon atom combined with the smallest number of hydrogen atoms. C. H. B.

Action of Methyl and Ethyl Alcohols on the Bromides of certain Propenyl Compounds. By F. J. Pond, E. S. Erb, and A. G. Ford (*J. Amer. Chem. Soc.*, 1902, **24**, 327—346).—When a solution of anethole dibromide in methyl alcohol is boiled for an hour in a reflux apparatus, hydrogen bromide is eliminated and an *additive* compound, $OMe{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CHMeBr$, of bromoanethole with methyl alcohol is obtained as a pale yellow, mobile oil which dissolves readily in alcohol, ether, chloroform, or acetic acid, and is decomposed by heat. If this oil is treated with sodium methoxide or ethoxide and the product boiled with hydrochloric acid, anisyl ethyl ketone is obtained. By the action of ethyl alcohol on anethole dibromide, the *compound*, $OMe{\cdot}C_6H_4{\cdot}CH(OEt){\cdot}CHBrMe$, is produced, and is converted by sodium ethoxide into anisyl ethyl ketone.

If bromoanethole dibromide is boiled with methyl alcohol, the *compound*, $OMe\cdot C_6H_3Br\cdot CH(OMe)\cdot CHMeBr$, is obtained which crystallises from acetone in large, colourless prisms, melts at 71—74°, and boils without decomposition at 160—164° under 14—15 mm. pressure; it does not decolorise permanganate solution or absorb bromine. By the action of sodium methoxide, it is converted into bromoanisyl ethyl ketone, first obtained by Hell and Hollenberg (Abstr., 1896, i, 354), which crystallises in long needles and melts at 100—101°; the *oxime* melts at 108°. The corresponding additive *compound* with ethyl alcohol, $OMe\cdot C_6H_3Br\cdot CH(OEt)\cdot CHMeBr$, is a mobile, amber-coloured oil which is converted by sodium ethoxide into bromoanisyl ethyl ketone.

The compounds formed by the action of methyl and ethyl alcohols on *iso*safrole dibromide were obtained as oils which could not be purified. By the action of sodium ethoxide on the methyl alcohol compound, a liquid is produced which yields an oxime identical with that obtained by the action of sodium methoxide on *iso*safrole dibromide (Wallach and Pond, Abstr., 1896, i, 95).

The *compound*, $CH_2{:}O_2{:}C_6H_2Br\cdot CH(OMe)\cdot CHMeBr$, obtained by the action of methyl alcohol on bromo*iso*safrole dibromide, crystallises in needles or prisms, melts at 75—76·5°, and is not affected by sodium methoxide. The corresponding *ethyl* compound forms large, rhombohedral crystals, melts at 58—60°, and is not affected by sodium ethoxide.

The *compound*, $CH_2{:}O_2{:}C_6Br(OMe)_2\cdot CH(OMe)\cdot CHMeBr$, formed by the action of methyl alcohol on bromo*iso*apiole dibromide, crystallises in large prisms and melts at 92°. The corresponding compound with ethyl alcohol was obtained as a dark-coloured, viscous oil.

The *compound*, $OEt\cdot C_6H_3(OMe)\cdot CH(OMe)\cdot CHMeBr$, obtained by the action of methyl alcohol on ethyl*iso*eugenol dibromide, crystallises from alcohol in colourless prisms and melts at 68°; another compound is simultaneously produced which crystallises in slender needles, melts at 128°, and does not contain bromine. E. G.

Hydrolysis of Glyceryl Tribenzoate. By LUIGI BALBIANO (*Gazzetta*, 1902, **32**, i, 265—279).—In confirmation of the views of Henriques (*Mon. Sci.*, 1898, [iv], **12**, 717), the author has shown that 1 mol. of sodium alkyloxide is sufficient to convert a glyceride such as glyceryl tribenzoate into glycerol according to the equation: $C_3H_5(OBz)_3 + NaOEt + EtOH + H_2O = C_3H_5(OH)_3 + C_6H_5\cdot CO_2Na + 2C_6H_5\cdot CO_2Et$. He further finds that the minimum proportion of sodium ethoxide necessary to bring about the complete hydrolysis of the tribenzoate by alcohol according to the equation: $C_3H_5(OBz)_3 + 3EtOH = C_3H_5(OH)_3 + 3C_6H_5\cdot CO_2Et$, is 1/50 gram-mol.; the presence of water is not required to bring about this reaction, which does not proceed step by step through mono- and di-glycerides but yields at once glycerol.

The opposing views of Geitel (Abstr., 1897, ii, 547) and of Lewkowitsch (Proc., 1899, 190) are discussed, and the author considers the theory advanced by Beilstein and Kossel concerning the mechanism of the action of sodium ethoxide on glyceryl tribenzoate to be the most likely one. T. H. P.

The Reaction between Acid Chlorides and Formaldehyde. By Marcel Descudé (*Compt. rend.*, 1902, **134**, 1065—1067).—It has already been proved (this vol., i, 339) that chloromethyl benzoate is formed when formaldehyde reacts with benzoyl chloride in presence of zinc chloride :—$C_6H_5 \cdot COCl + CH_2O = C_6H_5 \cdot CO_2 \cdot CH_2Cl$. Benzoic anhydride, dichloromethyl oxide, and methylene dibenzoate are also produced (compare Abstr., 1901, i, 357, 504). The reactions which take place are explained to be: $2C_6H_5 \cdot CO_2 \cdot CH_2Cl = (C_6H_5 \cdot CO)_2O + (CH_2Cl)_2O$ and $(C_6H_5 \cdot CO)_2O + CH_2O = (C_6H_5 \cdot CO_2)_2CH_2$.

With phthalyl chloride, formaldehyde gives dichloromethyl phthalate, phthalic anhydride, and dichloromethyl oxide, but no methylene diphthalate. A similar reaction takes place with acetyl chloride.

J. McC.

2-Chloro-3-aminobenzoic Acid. By Arnold F. Holleman [with G. L. Voerman] (*Rec. Trav. Chim.*, 1902, [ii], **21**, 56—58. Compare Abstr., 1901, i, 638).—On saturating with hydrogen sulphide an ammoniacal solution of 2-chloro-3-nitrobenzoic acid (*loc. cit.*), 2-chloro-3-aminobenzoic acid is obtained. It melts at 158°, whereas Griess (*Ber.*, 1886, **19**, 316) gives 185°, and has K 0·066.

m-Aminobenzoic acid was prepared from *m*-nitrobenzoic acid by reduction with ammonium sulphide and subsequent precipitation of the acid with tartaric acid—a method which gives a better yield than that recommended by Gerland (*Annalen*, 1834, **19**, 188). 2-Chloro-3-aminobenzoic acid could not be obtained from *m*-aminobenzoic acid by Griess's method. K. J. P. O.

Ethereal ω-Cyanomethylanthranilates. Badische Anilin- & Soda-Fabrik (D.R.-P. 129375).—ω-Cyanomethylanthranilic acid, when treated for a short time with mild esterifying agents, yields the corresponding esters without undergoing hydrolysis. Thus, methyl ω-cyanomethylanthranilate, $CN \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2Me$, can be obtained by the action of methyl alcohol and sulphuric acid, and the ethyl ester by that of ethyl alcohol and hydrochloric acid on the acid.

G. T. M.

Phenylglycine-*o*-carboxylic Acid. Daniel Vorländer and Rudolf von Schilling (D.R.-P. 127577. Compare Abstr., 1901, i, 710).—Nitroso-*o*-tolylglycine, prepared by the action of nitrous acid on *o*-toluidinediacetic acid, $C_6H_4Me \cdot N(CH_2 \cdot CO_2H)_2$, is oxidised by permanganate to nitrosophenylglycine-*o*-carboxylic acid, and may thus be employed in the production of indigo (compare Vorländer, Abstr., 1901, i, 463). G. T. M.

N-Alkyl Derivatives of Phenylglycine-*o*-carboxylic Acid. By Daniel Vorländer and Erich Mumme (*Ber.*, 1902, **35**, 1699—1701).—The N-alkyl derivatives of phenylglycinecarboxylic acid may be prepared by heating the aqueous solution of the sodium salt of the acid with an alkyl iodide. N-*Methylphenylglycinecarboxylic acid* melts and decomposes at about 189°. N-*Ethylphenylglycinecarboxylic acid* melts and decomposes at 184—186°; it has also been prepared from chloroacetic acid and ethylanthranilic acid. N-*Benzylphenylglycinecarboxylic acid* melts and decomposes at 190° after previously sintering. These acids are more strongly basic than phenylglycinecarboxylic acid itself, and show no characteristic reaction with fuming sulphuric acid. *Dimethyl* N-*methylphenylglycinecarboxylate*, prepared by direct esterification or by the action of dimethyl sulphate on phenylglycinecarboxylic acid or the N-methyl acid, melts at 82—83°. This substance, and the other normal esters of the N-alkylphenylglycinecarboxylic acids, are readily converted by alkalis and alkali carbonates into indoxyl derivatives. Methyl N-methylphenylglycinecarboxylate yields a mixture of two isomeric *methyl* N-*methylindoxylates*, one of which melts at 144—146°, and the other at about 88°. A. H.

Acyl Derivatives of Diethyl Phenylglycine-*o*-carboxylates.

Badische Anilin- & Soda-Fabrik (D.R.-P. 127648. Compare Abstr., 1901, i, 710).—*Diethyl formylphenylglycine-*o*-carboxylate*,

$$CO_2Et\cdot C_6H_4\cdot N(CHO)\cdot CO_2Et,$$

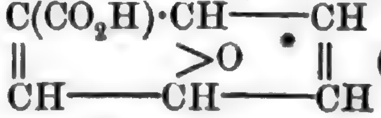
produced by heating diethyl phenylglycine-*o*-carboxylate with 90 per cent. formic acid at 150°, is readily soluble in most organic solvents and crystallises with great difficulty; the dimethyl ester also yields a *formyl* derivative.

*Diethyl benzoylphenylglycine-*o*-carboxylate*, $CO_2Et\cdot C_6H_4\cdot NBz\cdot CO_2Et$, obtained by the action of benzoyl chloride on the diethyl ester at 100°, is a viscid oil; the *benzoyl* derivative of the dimethyl ester is oily, but solidifies to a waxy mass on cooling.

*Triethyl phenylglycine-*o*-dicarboxylate*, $CO_2Et\cdot C_6H_4\cdot N(CO_2Et)_2$, results from the action of ethyl chloroformate on diethyl phenylglycine-*o*-carboxylate at 100°; it melts at 48°, boils with decomposition above 360°, and rapidly dissolves in the usual organic solvents. The corresponding trimethyl ester is a viscid, yellow oil boiling at 210—215° under 10 mm. pressure. G. T. M.

*iso*Salicylic Acid.

By **Heinrich Brunner** (*J. pr. Chem.*, 1902, [ii], 65, 304).—iso*Salicylic acid*,



(?), obtained by the action of aqua regia on an alcoholic solution of salicylic acid, crystallises in prisms and melts at 154°, but sublimes at a much lower temperature. The alkali salts are yellow and are converted into salicylates by continued action of alkalis. The *dibromo*-derivative crystallises in lemon-coloured prisms, forms red alkali salts, and is converted into dibromosalicylic acid when reduced with nascent hydrogen. R. H. P.

Oxidation of Anethole and Analogous Compounds containing a Propenylic Side Chain.

By **J. Bougault** (*Ann. Chim. Phys.*, 1902, [vii], 25, 483—574).—The greater portion of the work described in this memoir has already been published (compare Abstr., 1900, i, 311, 312, 361, 495, 548, 641; 1901, i, 324, 383, 389, 392, 721).

p-*Methoxyhydratropaldehyde*, $OMe\cdot C_6H_4\cdot CHMe\cdot COH$, obtained by the action of iodine and yellow mercuric oxide on anethole, is a colourless liquid boiling at 255—256° (corr.) and having a sp. gr. 1·069 at 15°; it is almost insoluble in water, and changes into resinous substances on treatment with concentrated acid or alkaline solutions. The *oxime*, when crystallised from ether, melts at 96°. *p*-Methoxyhydratropic acid, produced by oxidising the preceding aldehyde with silver nitrate in alkaline solution, crystallises in monoclinic prisms; its *ammonium* salt, $NH_4 \cdot C_{10}H_{11}O_3$, formed by passing ammonia into an ethereal solution of the acid, crystallises in leaflets readily soluble in water. The *sodium* salt, $C_{10}H_{11}O_3Na,2H_2O$, crystallises in needles, the *calcium* salt, $(C_{10}H_{11}O_3)_2Ca$, separates from water or dilute alcohol with $2H_2O$, the *lead* salt, $(C_{10}H_{11}O_3)_2Pb,H_2O$, forms white needles, the *silver* and *copper* salts are insoluble.

The acid contains an asymmetric carbon atom, and has been resolved into its optically active components by the aid of morphine, this alkaloid precipitating the lævorotatory acid in the form of a salt. The lævorotatory acid has $[\alpha]_D - 67°40'$; the dextrorotatory isomeride left in the mother liquors of the morphine salt was not obtained quite pure, the highest value for the rotatory power being $+55°$.

3 : 4-*Dimethoxyhydratropaldehyde*, $C_6H_3(OMe)_2 \cdot CHMe \cdot CHO$, obtained by the action of iodine and yellow mercuric oxide on methyl*iso*eugenol, is isolated in the form of its soluble bisulphite compound, and set free by boiling this derivative with sodium carbonate; it is soluble in the ordinary organic solvents and separates in crystals melting at 44°; the *oxime* melts at 77°.

3 : 4-*Dimethoxyhydratropic acid*, prepared from the preceding aldehyde, crystallises with $1H_2O$ and melts at 60°. The *sodium* salt, $C_{11}H_{13}O_4Na$, crystallises in colourless needles, the *calcium* salt is soluble in water and crystallises with $2H_2O$.

3 : 4-*Dihydroxyhydratropic acid*, $C_6H_3(OH)_2 \cdot CHMe \cdot CO_2H$, results from the action of red phosphorus and hydriodic acid and melts at 97°; in alkaline solution, it rapidly undergoes oxidation, giving a red coloration; ferric chloride develops a dark green coloration, changing to brown. 3 : 4-Dimethoxyacetophenone, $C_6H_3(OMe)_2 \cdot COMe$, is prepared by oxidising the corresponding dimethoxy-aldehyde or acid with chromic acid; it melts at 48° and on treatment with alkaline potassium permanganate gives rise to 3 : 4-dimethoxyphenylglyoxylic acid.

*iso*Apiole, on oxidation with iodine and yellow mercuric oxide, yields a *dimethoxymethylenedioxyhydratropaldehyde*,

$$CH_2{:}O_2{:}C_6H(OMe)_2 \cdot CHMe \cdot CHO,$$

a colourless liquid boiling at 305° and having a sp. gr. 1·246 at 15°; this compound is soluble in the ordinary organic solvents excepting light petroleum, and does not dissolve in water.

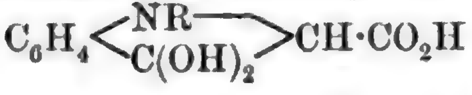
The corresponding *dimethoxymethylenedioxyhydratropic acid*,

$$CH_2{:}O_2{:}C_6H(OMe)_2 \cdot CHMe \cdot CO_2H,$$

obtained by oxidising the preceding compound with silver nitrate in alkaline solution, crystallises from water and melts at 97°; its sodium salt, $C_{12}H_{13}O_6Na,3H_2O$, is soluble in alcohol. The action of chromic mixture on the preceding aldehyde results in the formation of a *dimethoxymethylenedioxyacetophenone*, a substance crystallising from hot water in colourless needles, melting at 92°, and yielding dimethoxymethylenedioxyphenylglyoxylic acid on oxidation with alkaline permanganate.

G. T. M.

Isatoic Acid. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 127138).—Isatoic acid, $C_6H_4{<}\begin{array}{l}CO{-}O\\ NH{\cdot}CO\end{array}$, results from the action of hypochlorous acid on phthalimide in the absence of alkali hydroxides; it is precipitated by acidifying an emulsion of phthalimide and bleaching powder with dilute hydrochloric acid. The *sodium hydrogen* salt, $CO_2H{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2Na$, produced by dissolving phthalimide in dilute sodium hydroxide solution (1 mol. NaOH) and adding the equivalent amount of sodium hypochlorite solution, crystallises from this mixture in lustrous leaflets. G. T. M.

Formation of Indoxyl from Phenylglycine-*o*-carboxylic Acid. By Daniel Vorländer (*Ber.*, 1902, **35**, 1683—1698).—[With Erich Mumme and A. Wangerin.]—The production of indoxyl derivatives and indigo from the esters of phenylglycine-*o*-carboxylic acid by fuming sulphuric acid and by alkaline reagents appears to depend on stereochemical relations and not on the positive or negative character of the alkyl or acyl group which is introduced. It seems probable that an intermediate product of the type  $C_6H_4{<}\begin{array}{l}NR{-}{-}{-}\\ C(OH)_2\end{array}{>}CH{\cdot}CO_2H$ is first formed.

The following derivatives of phenylglycinecarboxylic acid have been employed. *Acetylphenylglycinecarboxylic acid* melts and decomposes at 214° after previously sintering; the electrical conductivity, *K* is 0·105 at 25°. The *benzoyl* derivative melts and decomposes at 195°. *Benzosulphurylphenylglycinecarboxylic acid* crystallises in plates and melts and decomposes at 190°. *Nitrosophenylglycinecarboxylic acid* melts and decomposes at about 120°. *Dimethyl acetylphenylglycinecarboxylate* melts at 81—82° and boils with slight decomposition at 205—212° under 30 mm. pressure. The *diethyl* ester melts at 63—64° and boils at 214—218° under 15 mm. pressure. The *monoethyl* ester (aliphatic) melts at 86—87° and has the conductivity *K* 0·038 at 25°; 2·40 grams dissolve in 100 of water at 13°. The *monoethyl* ester (aromatic) melts at 130—132° and has the conductivity *K* 0·030 at 25°, the solubility being 0·41 at 13°. *Diethyl propionylphenylglycinecarboxylate* melts at 64—66°. The *diethyl* ester of the *benzoyl* derivative forms an oil which crystallises after some time and then melts at 51—52°. *Diethyl carbethoxyphenylglycinecarboxylate,* prepared from ethyl chlorocarbonate, melts at 48—50°. *Diethyl nitrosophenylglycinecarboxylate* is an oil which gradually decomposes. The *methyl* ester of the *acetonitrilic acid,* prepared from the methyl ester of anthranilic acetonitrile, melts at 81—83°. The corresponding *ethyl* ester is an oil.

The reagents which bring about condensation to indoxyl derivatives may be divided into three classes.

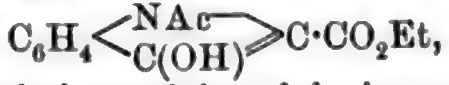
I. Reagents the effect of which is not much influenced by the degree of esterification or acylation. (1.) All derivatives of phenylglycinecarboxylic acid, except the nitroso-acid, its esters and benzosulphurylglycinecarboxylic acid, are converted into indoxylic acid and indoxyl by alkali hydroxides at temperatures above 200°. The presence of the alkali is essential, since neither the alkali salts nor the calcium or barium salts yield any indoxyl when heated alone. (2.) Boiling with acetic anhydride and sodium acetate has no effect on the nitroso-acid and the derivatives of anthranilic acetonitrile, but is applicable to all other derivatives. This reaction may be used as a test to distinguish phenylglycine-*o*-carboxylic acid from phenylglycine and from the *m*- and *p*-carboxylic acids. The acetyl derivative gives a better yield than the free acid, whilst the dialkyl esters only give very small yields. The benzosulphuryl derivative forms a diacylindoxyl which crystallises in flat needles melting at 142°.

II. Reagents the effect of which is increased by complete esterification of the phenylglycinecarboxylic acid derivatives. (3.) Aqueous alkalis and ammonia in the cold produce traces of indoxyl derivatives from the normal esters of acyl derivatives. These can be detected by the violet or blue coloration produced by boiling with 60 per cent. sulphuric acid. (4.) Boiling dilute aqueous alkalis and baryta water produce indoxyl derivatives from the normal acyl esters, but not from the free acids or the ester acids. The best yield is obtained with 20 per cent. aqueous potash. (5.) Boiling aqueous sodium carbonate also produces indoxyl derivatives, but in much smaller yield than the alkali hydroxides. (6.) Alcoholic aqueous alkali at the ordinary temperature only produces small amounts of indoxyl derivatives, the yield varying with the amount and the concentration of the alkali and with the percentage of alcohol. Excess of alkali tends to hydrolyse the esters rather than to produce condensation. (7.) Boiling alcoholic aqueous alkali produces larger yields. (8.) Alcoholic alkali or alcoholic sodium ethoxide at the ordinary temperature produces condensation to indoxylic esters, except with anthranilic acetonitrile and its acetyl derivative. *Diethyl N-acetylindoxylate* crystallises in needles melting at 114—115°; by the continued action of excess of alkali in the cold, it passes into indoxylic ester. *Diethyl N-benzoylindoxylate* melts at 84—86°, and does not lose the acyl group so readily as the acetyl compound. These two derivatives are isomeric with those obtained by the direct acylation of the indoxylic ester, and are soluble in cold aqueous alkalis. With ferric chloride, they give a permanent green coloration, whereas the *o*-acyl derivatives give no coloration, and the indoxylic esters themselves only a temporary green coloration with this reagent. Ethyl nitrosophenylglycinecarboxylate is converted by alcoholic sodium ethoxide into indoxylic ester. The non-acylated esters yield no indoxyl derivatives with alcoholic soda, and only traces with sodium ethoxide. (9.) Boiling alcoholic sodium ethoxide acts both on acylated and non-acylated derivatives, the best results being obtained when the solid ester is added to a concentrated alcoholic solution. Indoxylic acid may be prepared with advantage by this method from diethyl phenylglycinecarboxylate. (10.) In the presence of indifferent solvents, such as benzene or ether, the condensing action of sodium ethoxide is intensified, the reaction proceeding in the cold both with acylated and non-acylated derivatives. When treated with benzene, a small amount of alcohol and metallic sodium, the phenylglycinecarboxylic ester itself, and its benzoyl derivative readily undergo condensation, whereas the acetyl derivative in these circumstances yields no indoxyl compounds.

III. Reagents the effect of which is generally increased by acylation, but only slightly or not at all by esterification. (11.) When heated with anhydrous sulphuric acid or fuming sulphuric acid, the following compounds yield indigosulphonic acids: acetylphenylglycinecarboxylic acid, and its dimethyl, diethyl, and both monoethyl esters; diethyl propionylphenylglycinecarboxylate. On the other hand, the following do not yield indigo derivatives: phenylglycinecarboxylic acid and its esters, amides, and anilides; benzoylphenylglycinecarboxylic acid and its esters; the benzosulphuryl acid, the nitroso-acid and ester; the diethyl esters of the carbethoxy- and the formyl-acids, the anthranilic acetonitrile and its ester, and acetylanthranilic acetonitrile ester. This reagent may therefore be used as a test for the presence of acetyl- and propionyl-phenylglycinecarboxylic acids. The yield of indigo obtained from acetylphenylglycinecarboxylic acid is 49·7 per cent. of the theoretical, whilst that from the various esters is somewhat less. The reason for the difference between the behaviour of the acetyl and propionyl compounds on the one hand, and that of the benzoyl, formyl, carbethoxy-, and benzosulphuryl derivatives on the other, has not been ascertained. A. H.

Crystallised Indoxyl. By DANIEL VORLÄNDER and B. DRESCHER (*Ber.*, 1902, **35**, 1701—1702).—Indoxyl, which has hitherto been described as an uncrystallisable oil, can readily be obtained in yellow crystals by decomposing indoxylic acid with warm water in an atmosphere of coal gas, filtering, and cooling the solution in ice-water. It melts at 85°, is very sparingly soluble in light petroleum, and partially vaporises when heated alone or with slightly superheated steam, forming a vapour which has a fæcal odour. The analysis and determination of mol. weight by the cryoscopic method in benzene and acetic acid confirm the usual formula. A. H.

Ethereal Indoxylcarboxylates containing Acyl Groups attached to Nitrogen. FARBWERK MÜHLHEIM VORM. A. LEONHARDT (D.R.-P. 126962).—*Ethyl* N-*acetylindoxylcarboxylate*,



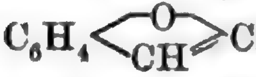
$$C_6H_4<\begin{matrix}NAc\\C(OH)\end{matrix}>C\cdot CO_2Et,$$

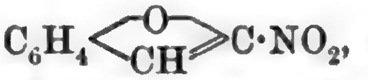
obtained by treating ethyl acetylphenylglycinecarboxylate with sodium ethoxide dissolved in absolute alcohol or with alcoholic potassium hydroxide at the ordinary temperature, crystallises out from the solution and melts at 115°. The *methyl* ester melts at 117°.

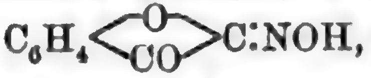
Ethyl N-*benzoylindoxylcarboxylate*, prepared from *ethyl benzoylphenylglycinecarboxylate* and sodium ethoxide, is obtained in yellow crystals melting at 87—88°. The glycine derivative itself is produced by heating diethyl phenylglycinecarboxylate with benzoyl chloride in toluene solution and melts at 53—54°.

The *urethanes*, $CO_2Et\cdot C_6H_4\cdot N(CO_2Me)\cdot CH_2\cdot CO_2Et$ and $CO_2Et\cdot C_6H_4\cdot N(CO_2Et)\cdot CH_2\cdot CO_2Et$, obtained by heating diethyl phenylglycinecarboxylate with excess of methyl and ethyl chlorocarbonates respectively, melt at 60—61° and 50°, and when treated with sodium ethoxide give rise to the corresponding urethanes of the alkyl indoxylcarboxylates. G. T. M.

Decomposition of Coumarone by means of Alcoholic Potassium Hydroxide. By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1902, **35**, 1630—1632. Compare Abstr., 1901, i, 533, 535).—Among the products of the decomposition of coumarone by alcoholic potassium hydroxide (*loc. cit.*), *o*-ethylphenol has now been recognised. It is present in the lowest fraction, obtained when the mixture of phenols is distilled under reduced pressure; it boils at 92—95° under 20 mm. pressure. The higher fractions appear to contain a polymeride of *o*-hydroxystyrene. In the products insoluble in alkali hydroxide, hydrocoumarone and a hydrocarbon, possibly tetrahydronaphthalene, were recognised. K. J. P. O.

1- and 2-Bromocoumarone. By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1902, **35**, 1633—1640).—1-Bromocoumarone,  $C_6H_4{<}^{O}_{CH}{\gg}CBr$, is prepared by the distillation of dibromocoumarone or by the action of phosphorus oxybromide on the lactone of *o*-hydroxyphenylacetic acid; the very pale yellow oil thus obtained boils at 220—222°, has a sp. gr. 1·5403 at 18°, and a refractive index 1·5986 at 22°. 2-Bromocoumarone, (m. p. 38—39°) was obtained by the action of alcoholic potash on dibromocoumarone. When heated under pressure at 190—200° with alcoholic potash, the liquid 1-bromocoumarone is quantitatively converted into *o*-hydroxyphenylacetic acid; 2-bromocoumarone yields only a small amount of *o*-hydroxyphenylacetic acid and *o*-ethoxyphenylacetic acid; at the same time, the presence of 2-ethoxycoumarone was rendered probable among the products of the reaction.

1-*Nitrocoumarone*,  $C_6H_4{<}^{O}_{CH}{\gg}C\cdot NO_2$, is formed when 1-bromocoumarone is exposed to the action of nitrous fumes, and is identical with the nitro-coumarone (Abstr., 1898, i, 30) obtained by the direct nitration of coumarone; it crystallises in white needles melting at 134°. By the action of nitrous fumes on 2-bromocoumarone, 2-bromonitrocoumarone (m. p. 132°) was obtained (*loc. cit.*). K. J. P. O.

1-Nitro-coumarone and one of its Characteristic Transformations. By RICHARD STOERMER and BRUNO KAHLERT (*Ber.*, 1902, **35**, 1640—1646. Compare preceding abstract).—On reducing an alcoholic solution of 1-nitrocoumarone with tin and hydrochloric acid, *o*-hydroxyphenylacetic acid is formed. When boiled with aqueous alkali hydroxides, 1-nitrocoumarone is converted into salicylic acid, hydrogen cyanide, and nitrous acid. If sodium ethoxide is employed, an intermediate product, *benzoximinoketolactone*,  $C_6H_4{<}^{O}_{CO}{>}C{:}NOH$, is obtained, which crystallises in white needles melting and decomposing at 172°, and is soluble in aqueous alkalis with an intense yellow colour. With phenylhydrazine, a *phenylhydrazoxime*, $C_{14}H_{11}O_2N_3$, is obtained as lemon-yellow crystals melting at 155—156°.

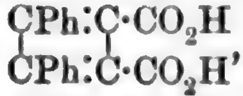
When an alkaline solution of the oximinoketolactone is boiled, salicylic acid is formed. By boiling hydrochloric acid, the oximinoketolactone is converted into hydroxylamine and *o*-hydroxybenzoylformic acid, to which the formula $OH{\cdot}C_6H_4{\cdot}CO{\cdot}CO_2H$ is assigned; it is found to melt at 39·5°; *o*-hydroxyphenyl*iso*nitrosoacetic acid, obtained from the benzoylformic acid, melted and decomposed at 149° (compare Baeyer and Fritsch, Abstr., 1884, 1021). K. J. P. O.

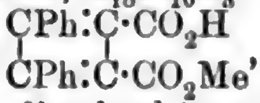
[6 : 6′-Dichloroindigotin.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 128727).—The presence of halogen radicles in the meta-positions with respect to the carbonyl groups of the indigo molecule does not affect the general properties and the colour of this pigment. If, however, chlorine atoms are introduced into the para-positions with respect to carbonyl, then a reddish-violet colouring matter is produced.

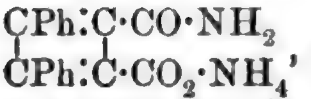
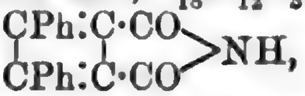
6 : 6′-*Dichloroindigotin*, prepared from *p*-chloro-*o*-nitrobenzaldehyde (m. p. 67—68°) by condensation with acetone in sodium hydroxide solution, is a brownish-red powder with a metallic lustre; it is insoluble in the ordinary solvents, but dissolves in boiling nitrobenzene or aniline to a deep red solution. Its vapour is deep red and on cooling yields the substance in a crystalline form. 6 : 6′-Dichloroindigotin, when treated with fuming sulphuric acid, forms a soluble sulphonic acid the barium salt of which is sparingly soluble. The dichloroindigotin may be treated in the ordinary indigo "vat," and gives reddish-violet shades on cotton and wool.

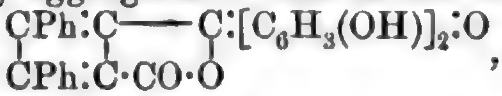
The intermediate *ketone*, $NO_2{\cdot}C_6H_3Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$, has also been isolated. G. T. M.

Diacetylindigo-white. DANIEL VORLÄNDER & BRUNO DRESCHER (D.R.-P. 126799. Compare Liebermann and Dickhuth, Abstr., 1892, 480).—Diacetylindigo-white is readily obtained in quantitative yield by shaking up an aqueous or acetone solution of a salt of indigo-white with acetic anhydride; it crystallises from water or acetone in white needles, becoming violet at 205° and decomposing at 215—230°. A *tetra-acetyl* derivative, which melts at 258°, is produced by warming the compound with acetic anhydride and sodium acetate. G. T. M.

Diphenyltetrenecarboxylic Acid. By THEODOR LANSER and B. F. HALVORSEN (*Ber.*, 1902, **35**, 1407—1411).—This acid is shown to have the constitution  $\begin{array}{l}\mathrm{CPh{:}C{\cdot}CO_2H}\\ \,|\qquad\ |\\ \mathrm{CPh{:}C{\cdot}CO_2H}\end{array}$, as assumed by Manthey (Abstr., 1901, i, 31), and is not a triphenyltrimesic acid, as previously supposed (Abstr., 1899, i, 916). The "partial anhydride," $C_{27}H_{16}O_5$, formerly described, is in reality the complete anhydride, $C_{18}H_{10}O_3$.

Monomethyl diphenyltetrenedicarboxylate,  $\begin{array}{l}\mathrm{CPh{:}C{\cdot}CO_2H}\\ \,|\qquad\ |\\ \mathrm{CPh{:}C{\cdot}CO_2Me}\end{array}$, obtained by hydrolysing the dimethyl ester with sodium dissolved in methyl alcohol, crystallises from alcohol in small, white needles and melts and decomposes at 207°; the *silver* salt, $C_{19}H_{13}O_4Ag$, is a white powder. The analogous *ethyl* ester, $C_{20}H_{16}O_4$, crystallises similarly and melts and decomposes at 207°. Both esters, when heated above the melting point, lose alcohol and yield the anhydride of the acid.

Attempts to prepare the amide of the acid failed, but on passing gaseous ammonia into a benzene solution of the anhydride, the *ammonium* salt,  $\begin{matrix}\mathrm{CPh{:}C{\cdot}CO{\cdot}NH_2}\\ \mathrm{CPh{:}C{\cdot}CO_2{\cdot}NH_4}\end{matrix}$, of the acid amide is obtained as a white, voluminous precipitate; the analogous *silver* salt, $C_{18}H_{12}O_3NAg$, was analysed. *Diphenyltetrenedicarboxylimide,*  $\begin{matrix}\mathrm{CPh{:}C{\cdot}CO}\\ \mathrm{CPh{:}C{\cdot}CO}\end{matrix}\!>\mathrm{NH}$, obtained by subliming the anhydride in dry ammonia, crystallises from alcohol in feathery aggregates of needles and melts at 246°.

The *fluorescein,*  $\begin{matrix}\mathrm{CPh{:}C\text{——}C{:}[C_6H_3(OH)]_2{:}O}\\ \mathrm{CPh{:}C{\cdot}CO{\cdot}O}\end{matrix}$, obtained from diphenyltetrenecarboxylic acid by fusing its anhydride with resorcinol, crystallises from toluene. W. A. D.

Some Amyl Esters of Substituted Phthalic Acids. By Wilhelm Marckwald (*Ber.*, 1902, **35**, 1602—1606).—1-*iso*Amyl hydrogen 3-nitrophthalate melts at 93·5°, and again melts at the same point if solidified only a few degrees below this temperature; if, however, the liquid be cooled rapidly to 70°, it solidifies, and the product melts and remelts at 78°, the melting point only rising to 93·5° after the solid mass has been left for several hours. The ester is thus dimorphous, and melting point curves are given which show that the labile form melting at 78° is isomorphous with the isomeric 1-*d*-amyl hydrogen 3-nitrophthalate; as, however, the labile form is not produced in quantity when the inactive ester is prepared from *iso*amyl alcohol containing 20 per cent. of the active alcohol, a single crystallisation of the product effects a complete separation.

2-*iso*Amyl hydrogen 3-nitrophthalate melts at 161—162°, 4° lower than stated by McKenzie (Trans., 1901, **79**, 1135); 2-d-*amyl hydrogen 3-nitrophthalate,* obtained by heating 3-nitrophthalic anhydride with pure *d*-amyl alcohol, crystallises from benzene in silvery leaflets, melts at 154—155°, and has $[\alpha]_D$ +2·6 in acetone solution. A curve is given showing the melting points of mixed crystals of the *iso*amyl and *d*-amyl esters.

iso*Amyl hydrogen tetrachlorophthalate* crystallises from carbon disulphide in stout, vitreous prisms, and melts at 112—113°; the analogous d-*amyl ester* separates from light petroleum in opaque crystals and melts at 94—95°. In spite of their solubility in light petroleum being very different, the salts are only separated with great difficulty by crystallisation from this solvent owing to the formation of mixed crystals; a curve is given showing the variation in the melting point of such crystals. W. A. D.

Unsaturated Dicarboxylic Acids from Ketones and Diethyl Succinate. By Hans Stobbe (*Annalen*, 1902, **321**, 83—93. Compare Abstr., 1899, i, 900, 901, 902; 1900, i, 179; 1901, i, 149, 276, 549, and succeeding abstracts).—A theoretical discussion of the experimental results indicated in the two following abstracts, from which the following rules are deduced.

1. In condensing ketones with diethyl succinate, γδ-unsaturated acids (alkylidenepyrotartaric acids) are the principal products when the

ketones contain the methylene radicle, whereas ketones in which this group is absent give rise to βγ-acids (substituted itaconic acids).

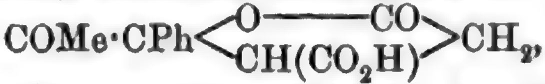
2. The tendency to form alkylidene pyrotartaric acids is greater in the ketones containing a methylene residue combined with an aromatic nucleus than in those in which methylene is attached to aliphatic radicles. G. T. M.

Condensation of Propiophenone with Diethyl Succinate.

By Hans Stobbe and Karl Niedenzu (*Annalen*, 1902, **321**, 94—100. Compare preceding abstract).—*γ-Phenyl-γ-ethylidenepyrotartaric acid*, $CHMe\colon CPh\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, produced by condensing propiophenone with ethyl succinate in the presence of sodium ethoxide suspended in dry ether, is isolated in the form of its *barium* salt, $C_{13}H_{12}O_4Ba$, a substance which crystallises in silky, colourless needles. The free acid crystallises from hot water in colourless, monoclinic needles readily soluble in the ordinary organic solvents excepting light petroleum and carbon disulphide; it melts at 137—138°. The *calcium* salt, $C_{13}H_{12}O_4Ca,H_2O$, is a crystalline powder, the *silver* salt, $C_{13}H_{12}O_4Ag_2$, a curdy precipitate.

When oxidised with 3 atoms of oxygen derived from potassium permanganate, the preceding acid gives rise to β-benzoylpropionic and acetic acids together with a trace of benzoic acid.

γ-Acetyl-γ-phenylbutyrolactone-β-carboxylic acid,



$$COMe\cdot CPh{<}\begin{matrix}O\text{———}CO\\ CH(CO_2H)\end{matrix}{>}CH_2,$$

is also produced in the preceding oxidation, but is obtained in better yield when only 2 atoms of oxygen are employed; it crystallises from water containing a few drops of sulphuric acid in well-defined monoclinic prisms melting at 141—142°. The existence of a lactone ring in this acid is demonstrated by titrations with *N*/10 hydrochloric acid and potassium hydroxide. The *barium* salt, $(C_{13}H_{11}O_5)_2Ba$, of the lactone-acid is soluble in absolute alcohol, whilst the *barium* salt, $C_{13}H_{12}O_6Ba$, of the hydroxy-dicarboxylic acid is insoluble in this medium; the latter substance results from the fission of the lactone ring and they are both obtained on treating the lactone-acid with freshly precipitated barium carbonate.

The *semicarbazone*, $C_{14}H_{15}O_5N_3$, of the lactone-acid produced by the action of semicarbazide hydrochloride and sodium acetate separates from dilute alcohol in granular crystals decomposing at 210°. Prolonged treatment of the lactone-acid with permanganate solution leads to the production of benzoylpropionic and acetic acids.

Two stereoisomeric substances, *γ-phenyl-γ-ethylitaconic acid* and *γ-phenyl-γ-ethylisoitaconic acid*, are obtained in the condensation of propiophenone and ethyl succinate, and are isolated in the mother liquors after the separation of the substituted pyrotartaric acid.

γ-Phenyl-γ-ethylitaconic acid, $CEtPh\colon C(CO_2H)\cdot CH_2\cdot CO_2H$, crystallises from hot water in triclinic prisms and decomposes at 175—176°; it is sparingly soluble in water or benzene, and is separated from its isomeride by fractional crystallisation from these solvents. The *calcium* salt, $C_{13}H_{12}O_4Ca$, is a granular precipitate.

γ-Phenyl-γ-ethylisoitaconic acid separates from its aqueous solution in comb-like aggregates of triclinic plates decomposing at 184—184·5°; the crystals differ entirely from those of the stereoisomeride in shape, and in angle of extinction. The *calcium* salt is described.

The two stereoisomeric acids, when oxidised with potassium permanganate in sodium carbonate solution, yield the same products, namely, propiophenone with traces of acetic and oxalic acids.

G. T. M.

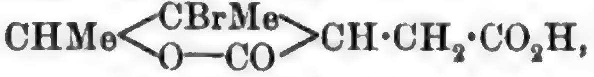
Condensation of Methyl Ethyl Ketone with Ethyl Succinate

By Hans Stobbe, Arthur Strigel, and Carl Meyer (*Annalen*, 1902, **321**, 105—126).—*γ-Methyl-γ-ethylidenepyrotartaric acid*,

$$CHMe{:}CMe{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H,$$

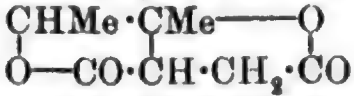
formerly called methylethylaticonic acid (compare Abstr., 1895, i, 143), is the chief product of the condensation between methyl ethyl ketone and ethyl succinate; its electrical conductivity, μ_∞, is 351, and its dissociation constant, K, is 0·0112. The normal *potassium* salt, $C_8H_{10}O_4K_2$, crystallises in lustrous spangles, the *potassium hydrogen* salt, $C_8H_{11}O_4K,H_2O$, separates from dilute alcohol in well-defined, rhombic plates. When treated with an alkaline solution of potassium permanganate, the acid yields a mixture of lævulic and acetic acids, about 20 per cent. of the original substance remaining unchanged.

β-Bromo-βγ-dimethylbutyrolactoneacetic acid,



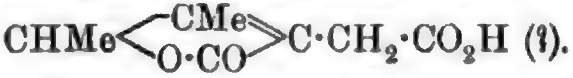
$$CHMe<\begin{matrix}CBrMe\\O—CO\end{matrix}>CH{\cdot}CH_2{\cdot}CO_2H,$$

formerly known as γ-methyl-γ-ethyl-β-bromoparaconic acid, results from the action of bromine on the preceding acid dissolved in chloroform; it melts at 161°, and when left in contact with cold sodium hydroxide solution, or when boiled with this reagent, gives rise to the *dilactone*,



$$\begin{matrix}CHMe{\cdot}CMe—O\\ |\qquad\quad |\qquad\quad |\\O—CO{\cdot}CH{\cdot}CH_2{\cdot}CO\end{matrix}$$

, *γδ-dihydroxy-γ-methyl-γ-ethylpyrotartaric acid*, and *βγ-dimethylcrotonolactoneacetic acid*,

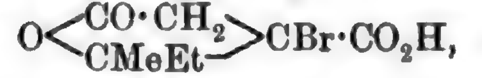


$$CHMe<\begin{matrix}CMe\\O{\cdot}CO\end{matrix}>C{\cdot}CH_2{\cdot}CO_2H\ (?).$$

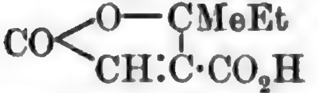
The former of these substances is insoluble in sodium carbonate solution but dissolves readily in hot water or chloroform, and more sparingly in carbon disulphide or ether; it separates in rhombic crystals and melts at 147—148°. When treated with potassium hydroxide, the dilactone reacts as a hydroxymonolactonecarboxylic acid, only one of the lactone rings undergoing fission. Excess of barium hydroxide solution (3 mols.) leads to the disruption of both lactone rings, the *barium* salt obtained having the composition $C_6H_{10}(OH)_2(CO_2)_2Ba$. βγ-Dimethylcrotonolactoneacetic acid, the chief product of the hydrolysis of the bromo-acid, separates from ether in short prisms or plates and melts at 144—145°. γ-Methyl-γ-ethylitaconic acid,

$$CMeEt{:}C(CO_2H){\cdot}CH_2{\cdot}CO_2H,$$

the bye-product of the condensation between methyl ethyl ketone and ethyl succinate, is less soluble than γ-methyl-γ-ethylidenepyrotartaric acid, and is purified by crystallisation from acetone; it melts and decomposes at 181°. Its electrical conductivity, μ_∞, is 351, the calculated dissociation constant, K, being 0·0150. The substance may be titrated as a dibasic acid; the *barium* salt, $C_8H_{10}O_4Ba$, crystallises in small plates and the silver salt is a flocculent, white precipitate soluble in hot water and sensitive to light. On oxidation with alkaline permanganate solution, the acid yields a mixture of oxalic and acetic acids with methyl ethyl ketone. *β-Bromo-γ-methyl-γ-ethylparaconic acid*,



$\mathrm{O}<\begin{matrix}\mathrm{CO\cdot CH_2}\\ \mathrm{CMeEt}\end{matrix}>\mathrm{CBr\cdot CO_2H}$, results from the action of bromine on an aqueous suspension of the preceding acid; it crystallises from benzene in silky needles decomposing at 163°. *γ-Methyl-γ-ethylaconic acid*,



$\mathrm{CO}<\begin{matrix}\mathrm{O-\overset{}{C}MeEt}\\ \mathrm{CH{:}\underset{}{C}\cdot CO_2H}\end{matrix}$, obtained on warming the preceding compound with sodium hydroxide solution, crystallises from water in lustrous scales melting at 117—119°; it is readily soluble in the ordinary organic solvents, and its alkaline solution decolorises permanganate. The lactone ring in this substance is very stable; the acid is exactly neutralised by one equivalent of potassium hydroxide, and the *barium* salt, $(C_8H_9O_4)_2Ba$, obtained by the action of excess of barium hydroxide, shows that the compound is a monobasic acid. Fission of the lactone ring occurs only on boiling the acid with excess of alkali hydroxide solution. A rapid titration of the solution with standard acid indicates that the neutralisation of the free alkali induces the regeneration of the lactone so that the neutralised solution is again rendered alkaline, the alkalinity increasing rapidly when the solution is allowed to remain for some time before the final titration. An exactly neutralised solution is found to contain after 24 hours 95·70 per cent. of the lactone-acid, and only 4·30 per cent. of the hydroxy-dicarboxylic acid. The volumetric results and the properties of the two unsaturated dicarboxylic acids and their derivatives are summarised in tabular form.

Ethyl hydrogen γ-methyl-γ-ethylitaconate,

$$\mathrm{CMeEt{:}C(CO_2Et)CH_2\cdot CO_2H},$$

is obtained as an oil on distilling in steam the products of the condensation; it is accompanied by a certain quantity of the free acid, the two substances being separated by the difference in solubility of their potassium salts in absolute alcohol. The salt of the acid-ester dissolves in this solvent, whilst the potassium methylethylitaconate is insoluble. The acid ester boils at 171—177° under 15 mm. pressure and is very unstable, being converted into the corresponding acid. The *barium* salt, $(CO_2Et\cdot C_6H_{10}\cdot CO_2)_2Ba$, is amorphous and soluble in water or alcohol.

G. T. M.

Separation of Phenylparaconic Acid into its Optically Active Components. By AD. KREUTZ (*Annalen*, 1902, **321**, 127—139).—l-*Phenylparaconic acid*, $C_{11}H_{10}O_4$, obtained from the strychnine salt, which is precipitated by the addition of the finely powdered alkaloid to a solution of *r*-phenylparaconic acid (m. p. 99°) in absolute alcohol, crystallises from water in flexible needles and from the organic solvents in lustrous leaflets; it separates with ¼ mol. H_2O, like the racemic compound, and melts indefinitely at 125—131°. The acid has $[\alpha]_D$ −59·3° in dilute alcohol; the *strychnine* salt is sparingly soluble in cold water or alcohol, but dissolves more readily in hot water; it softens at 198° and melts at 202—203°. The calcium salt, $(C_{11}H_9O_4)_2Ca$, crystallises in needles; the *barium* salt separates in needles containing $3H_2O$; the *silver* salt is stable to light and forms druses of small needles. *Sodium* l-*phenylparaconate* has $[\alpha]_D$ $-53{\cdot}11°$, whilst the *sodium* salt of the corresponding hydroxy-acid (l-phenylitamalic acid) has $[\alpha]_D$ $-17{\cdot}19°$; the free hydroxy-acid set free in ice-cold solutions has $[\alpha]_D$ $-12{\cdot}29°$. The hydroxy-acid and its salt are therefore much less active than the corresponding lactone derivatives.

d-*Phenylparaconic acid* is obtained in the form of its strychnine salt from the final mother liquor obtained in crystallising strychnine l-phenylparaconate; the free acid, $C_{11}H_{10}O_4, \frac{1}{4}H_2O$, resembles its optical antipode and melts between 115° and 131°; it has $[\alpha]_D$ $+56{\cdot}9°$ in 50 per cent. alcohol. The *strychnine* salt separates in ill-defined crystals melting at 100—102°; the *barium, calcium,* and *silver* salts closely resemble those of the lævorotatory acid.

Sodium d-*phenylparaconate* and *sodium* d-*phenylitamalate* have $[\alpha]_D$ $+57{\cdot}35°$ and $+25{\cdot}15°$ respectively. *Barium* d-*phenylitamalate*, $C_{11}H_{10}O_5Ba$, crystallises from hot water with $1H_2O$; the optically active phenylparaconic acids behave like the racemic compound on distillation and give rise to phenyl*iso*crotonic acid and α-naphthol. G. T. M.

Esters of Phloroglucinolcarboxylic Acids. By Josef Herzig and Franz Wenzel [and, in part, Rudolf Tölk and Bruno Graetz] (*Monatsh.*, 1902, **23**, 81—118. Compare Abstr., 1901, i, 473).—The action of diazomethane on phloroglucinolcarboxylic acid in ethereal solution leads to the formation of methyl phloroglucinolcarboxylate and methyl methoxy-, dimethoxy-, and trimethoxy-phloroglucinolcarboxylates. Methyl phloroglucinolcarboxylate is now found to melt at 174—176°. The methyl methoxyphloroglucinolcarboxylate is identical with that previously described. *Methyl dimethoxyphloroglucinolcarboxylate*, $OH{\cdot}C_6H_2(OMe)_2{\cdot}CO_2Me$, crystallises from methyl alcohol in colourless needles and melts at 107—109°. Methyl trimethoxyphloroglucinolcarboxylate, $C_6H_2(OMe)_3{\cdot}CO_2Me$, is best prepared by the action of methyl iodide and potassium hydroxide on methyl dimethoxyphloroglucinolcarboxylate; it crystallises in white needles and melts at 67—70°. It is also formed along with a small quantity of dimethoxyphloroglucinol and a substance melting at 185—187°, which may be methyl dimethoxyphloroglucinoldicarboxylate, by the action of methyl chlorocarbonate on trimethoxyphloroglucinol in presence of aluminium chloride.

Dimethoxyphloroglucinolcarboxylic acid, $OH{\cdot}C_6H_2(OMe)_2{\cdot}CO_2H$, is prepared by the hydrolysis of its methyl ester by concentrated sulphuric acid at 80°, or by dilute alcoholic potassium hydroxide; it forms colourless needles which decompose at 152—154°. It is also formed by heating the sodium derivative of dimethoxyphloroglucinol with carbon dioxide under pressure.

Methyl trimethoxyphloroglucinolcarboxylate evolves carbon dioxide when treated with concentrated sulphuric acid. It may be hydrolysed by the action of metallic sodium in xylene solution. *Trimethoxyphloroglucinolcarboxylic acid* crystallises from alcohol in colourless needles which melt with decomposition at 140—141°. The action of diazomethane on methylphloroglucinolcarboxylic acid leads to the formation of methyl methylphloroglucinolcarboxylate and methyl methoxymethylphloroglucinolcarboxylate.

Methyl methylphloroglucinolcarboxylate, $C_6HMe(OH)_3{\cdot}CO_2Me$, melts at 144—145°; with sodium acetate and acetic anhydride, it yields a *triacetyl* derivative which melts at 103—104°. Hydrolysis of the triacetyl derivative by concentrated sulphuric acid results apparently in polymerisation (compare Abstr., 1899, i, 31). *Methyl methoxymethylphloroglucinolcarboxylate*, $OMe{\cdot}C_6HMe(OH)_2{\cdot}CO_2Me$, melts at 132—133°; it yields a *diacetyl* derivative which melts at 75—77°.

When dimethylphloroglucinolcarboxylic acid is treated with diazomethane, it yields methyl dimethylphloroglucinolcarboxylate and *methyl methoxydimethylphloroglucinolcarboxylate*, $OMe{\cdot}C_6Me_2(OH)_2{\cdot}CO_2Me$, which melts at 96—98°, and on hydrolysis by dilute alcoholic potassium hydroxide yields *methoxydimethylphloroglucinolcarboxylic acid*, melting with evolution of carbon dioxide at 156—157°.

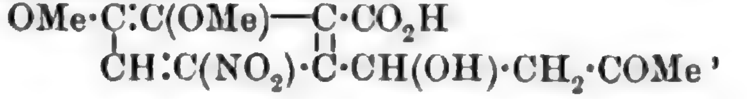
Methoxydimethylphloroglucinol, formed by boiling the carboxylic acid with water, or by hydrolysis of the methyl ester by an excess of potassium hydroxide, melts at 147—148°. Being isomeric with Bosse's dimethylphloroglucinol methyl ether (Abstr., 1901, i, 207), it must have the constitution $[Me_2 : OMe : (OH)_2 = 1 : 3 : 2 : 4 : 6]$.

Methyl dimethylphloroglucinolcarboxylate is formed by the action of methyl iodide on silver methylphloroglucinolcarboxylate or on silver dimethylphloroglucinolcarboxylate; in the latter case, no methylation of the benzene nucleus takes place.

Methoxyphloroglucinolcarboxylic acid and methyl iodide, in presence of a slight excess of sodium methoxide, yield *methoxymethylphloroglucinolcarboxylic acid*, which melts, with evolution of carbon dioxide, at 147°. When boiled with water, the acid loses carbon dioxide, and yields a methoxymethylphloroglucinol, which is identical with that described by Boehm (Abstr., 1899, i, 32), and has the constitution $[OMe : Me : (OH)_2 = 1 : 2 : 3 : 5]$.

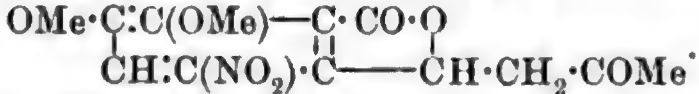
By further treatment of methoxymethylphloroglucinolcarboxylic acid with methyl iodide and sodium methoxide, there are obtained its methyl ester, a substance melting at 205—207°, which is probably Boehm's methyl ether of filicic acid (Abstr., 1899, i, 804), and a thin syrup which, on standing, deposits crystals of methoxytetramethylphloroglucinol, and on hydrolysis with excess of potassium hydroxide yields tetramethylphloroglucinol. G. Y.

Action of Acetone on Nitro-opianic Acid. By G. Book (*Ber.*, 1902, **35**, 1498—1502. Compare Liebermann, Abstr., 1886, 468).—*Acetonylnitromeconin*, produced together with tetramethoxyindigotindicarboxylic acid (opianindigo) by the action of acetone on nitro-opianic acid, is separated from the sodium salt of the indigo derivative by dissolving the latter in cold water; it crystallises in pale yellow needles and melts at 175°. The initial product of the condensation is probably acetonylnitromeconic acid,



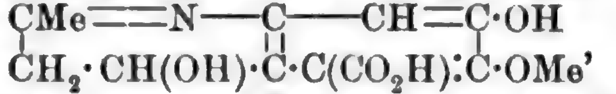
$$\begin{array}{l} \mathrm{OMe{\cdot}C{:}C(OMe){-}C{\cdot}CO_2H} \\ \quad\;\mathrm{CH{:}C(NO_2){\cdot}C{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe} \end{array},$$

this substance which has not yet been isolated being the parent compound both of opianindigo and acetonylnitromeconine. The latter derivative, being formed by the elimination of water, has the constitution indicated by the formula



$$\begin{array}{l}\mathrm{OMe{\cdot}C{:}C(OMe){-}C{\cdot}CO{\cdot}O} \\ \mathrm{CH{:}C(NO_2){\cdot}C{=\!=}CH{\cdot}CH_2{\cdot}COMe}\end{array}.$$

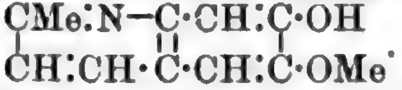
Dihydroxymethoxydihydroquinaldinecarboxylic acid,



$$\begin{array}{l}\mathrm{CMe{=\!=}N{-}C{-}CH{=}C{\cdot}OH} \\ \mathrm{CH_2{\cdot}CH(OH){\cdot}C{\cdot}C(CO_2H){:}C{\cdot}OMe}\end{array},$$

produced by reducing the preceding compound with tin and hydrochloric acid, is obtained as a white, granular precipitate melting at 212°; it has both basic and acidic properties, dissolving in alkaline and ammoniacal solutions and yielding an aurichloride and a crystalline platinichloride. The formation of this substance is attended by the reduction of the nitro-group and the elimination of one methyl radicle in the form of methyl chloride.

When a solution of the preceding acid is repeatedly evaporated to dryness with hydrochloric acid, the final residue consists of the *hydrochloride* of a new *hydroxymethoxyquinaldine*,



$$\begin{array}{l}\mathrm{CMe{:}N{-}C{\cdot}CH{:}C{\cdot}OH} \\ \mathrm{CH{:}CH{\cdot}C{\cdot}CH{:}C{\cdot}OMe}\end{array}.$$

The *platinichloride* of this base crystallises from water in long, yellow needles.

G. T. M.

Compounds from Lichens. IX. By WILHELM ZOPF (*Annalen*, 1902, **321**, 37—61. Compare Abstr., 1901, i, 87, 547).—*Lecidea confluens*, unlike so many other lichens, seems to contain only one acidic substance, namely, confluentin (m. p. 147—148°). The name *picrolichenic acid* is suggested for picrolichenin; this substance melts at 178°, dissolves in solutions of the alkali carbonates, being reprecipitated by acids; it readily gives rise to resinous products, even in alcoholic solution, at the ordinary temperature. *Pertusaria lactea*, found at high altitudes in Tessin and the Tyrol, yields lecanoric acid and a new compound, *variolaric acid*, which is obtained only in very small amount; it melts at 285°, and develops violet and orange-red colorations with ferric chloride and calcium hypochlorite respectively. Rhizocarpic and pleopsidic acids are obtained from *Acarospora chlorophana*, the latter substance crystallising in tetragonal pyramids. *Hæmatomma coccineum* (var. *leiphæmum*), a greyish-white or green lichen, seems to be a distinct variety of the yellow *H. coccineum*, for it does not yield any usnic acid, and furnishes a new compound, *leiphæmum*, which melts at 193°, and is insoluble in alkali hydroxide solutions. Both varieties contain atranoric acid and zeorin.

Parmelia glomellifera contains a new substance, *glomelliferin*, which crystallises in rosettes of white needles and slowly decomposes in benzene solution, giving rise to *glomellic acid* and a compound having the properties of sphærophorin. The new acid melts at 123—124°, and crystallises from chloroform in short plates or prisms and from benzene in druses of fusiform crystals; it dissolves in solutions of the alkali hydroxides and carbonates and develops a violet coloration with ferric chloride. Glomelliferin is also decomposed by cold potassium hydroxide solution into glomellic acid and a substance giving a red coloration with calcium hypochlorite and melting at 141°; another compound, *glomellin*, is also isolated among the products of this hydrolysis; it crystallises in rhombic plates and melts at 92°.

Olivetoric acid, obtained from *Parmelia olivetorium*, melts at 141—142°, and gives rise to a characteristic colour reaction with barium peroxide solution, first becoming lemon-yellow and then green without dissolving in the reagent. Lecanoric acid, which has been confounded with this compound, melts at 166° and dissolves in barium peroxide solution without developing any coloration. Moreover, when heated with methyl alcohol at 150°, lecanoric acid yields methyl orsellate (m. p. 128°), whilst olivetoric acid gives rise to a substance melting below 100° which still gives the barium peroxide reaction (compare Hesse, Abstr., 1901, i, 149).

Parmelia perlata, which gives rise to atranoric and hæmatommic acids, also furnishes a third acid which is identical with the imbricaric acid formerly obtained from *P. lacarnensis*. When pure, this acid crystallises in obliquely truncated prisms and melts at 115°.

G. T. M.

[Derivatives of] *p*-Chlorobenzaldehyde. By Reinhold von Walther and W. Raetze (*J. pr. Chem.*, 1902, [ii], **65**, 258—290).—*p*-Chlorobenzaldehyde was obtained from *p*-aminobenzaldehyde by Sandmeyer's reaction and its reactions compared with those of benzaldehyde. Neither the formation of a chlorobenzoin nor a chlorohydrobenzamide was observed, although the action of ammonia on the chlorobenzaldehyde produced a very unstable *compound* melting at 86—90°. The following condensation compounds with amines are described.

p-*Chlorobenzylideneaniline* forms yellow, slender leaflets melting at 62°. p-*Chlorobenzylidene*-p-*toluidine* crystallises in lustrous white leaflets melting at 125°. p-*Chlorobenzylidene*-m-*toluidine* forms leaflets melting at 32°. p-*Chlorobenzylidene-o-toluidine* forms needles melting at 35·5°. p-*Chlorobenzylidene*-p-*chloroaniline* crystallises in yellow needles or lustrous leaflets and melts at 112°. p-*Chlorobenzylidene*-m-*chloroaniline* forms felted needles melting at 67°. *Di*-p-*chlorobenzylidenebenzidine* forms yellowish laminæ melting at 264°. *Di*-p-*chlorobenzylidene*-p-*phenylenediamine* crystallises in leaflets and melts at 200°.

p-*Chloromandelonitrile* is a yellow oil. p-*Chlorophenyl-a-chloroacetic acid* crystallises in white leaflets and melts at 118°. The nitrile condenses with amines, forming the following compounds, which can be also obtained by the addition of hydrogen cyanide to the Schiff's bases previously described. m-*Chloroanilino-a*-p-*chlorophenylacetonitrile*, $C_6H_4Cl·NH·CH(C_6H_4Cl)·CN$, forms small leaflets melting at 88°. *Anilino-a*-p-*chlorophenylacetonitrile*, crystallises in slender, white needles and melts at 112°; the corresponding *amide* forms microscopic needles melting at 145°, and the *acid* crystallises in small, slender needles melting and decomposing at 202°. *a*-p-*Toluidino*-p-*chlorophenylacetonitrile* forms small, white leaflets melting at 80°; the corresponding *amide* crystallises in slender, white needles melting at 132°, and the *acid* in leaflets melting and decomposing at 186°. *a*-m-*Toluidino*-p-*chlorophenylacetonitrile* forms white, lustrous leaflets melting at 105°; the corresponding *amide* is a crystalline powder which melts at 137—138°; the *acid* is a crystalline powder melting and decomposing at 180°. α-o-*Toluidino*-p-*chlorophenylacetonitrile* forms colourless needles melting at 106°; the corresponding *amide* forms white, felted needles melting at 127°. o-*Carboxyanilino-α-phenylacetonitrile* crystallises in yellow needles, melts and decomposes at 166°; the corresponding *amide* is a yellowish powder melting at 236°, and the *acid* a white, crystalline powder melting and decomposing at 184—186°. *Benzidinedi*-p-*chloromandelonitrile* is a yellow, crystalline powder melting at 237°. p-*Phenylenediaminodi*-p-*chlorobenzyl cyanide* melts at 190°.

The aldehyde condenses with acetone, forming p-*chlorobenzylideneacetone*, which crystallises in white needles, melts at 50—51°, and yields a *phenylhydrazone* melting at 160°, and an *oxime* crystallising in slender, white needles. p-*Chlorobenzylideneacetophenone* crystallises in yellow needles, melts at 103—104°, and yields an *oxime* melting at 153°.

p-Chlorobenzaldehyde condenses with benzyl cyanide in the presence of sodium ethoxide, forming *α-phenyl*-p-*chlorocinnamonitrile*, which crystallises in silky leaflets melting at 108°, and when treated with sodium in alcoholic solution yields dibenzyl. *α*-p-*Nitrophenyl*-p-*chlorocinnamonitrile* crystallises in slender, yellow needles melting at 180°. When heated with phenylacetic acid, *p*-chlorobenzaldehyde yields p-*chlorostilbene*, which crystallises in lustrous white leaflets melting at 127°; when treated with ethyl cyanoacetate and sodium ethoxide, it yields *ethyl α-cyano*-p-*chlorocinnamate*, which melts at 93°, and when hydrolysed yields the *acid* melting at 196°; the corresponding *methyl* ester crystallises in slender, felted needles and melts at 121°.

Ethyl 4-p-*chlorophenyldihydrolutidinedicarboxylate*, obtained by the condensation of *p*-chlorobenzaldehyde (1 mol.) with ethyl acetoacetate (2 mols.) and ammonia, crystallises in compact tablets melting at 147°, and when oxidised by nitrous acid yields *ethyl* 4-p-*chlorophenyl-lutidinedicarboxylate*, which crystallises in long, white needles melting at 67°, and when hydrolysed gives the *acid*, which is an insoluble powder, melting at 274°. R. H. P.

Atmospheric Oxidation of *m*-Hydroxybenzaldehydephenylhydrazone and its Derivatives. By HEINRICH BILTZ and OTTO KAMMANN (*Annalen*, 1901, **321**, 32—37. Compare next page).—When oxidised by a current of air in alcoholic potassium hydroxide solution, *m*-hydroxybenzaldehydephenylhydrazone gives rise to tarry products.

2 : 4 : 6-*Trichloro-3-hydroxybenzaldehydephenylhydrazone* crystallises from dilute alcohol in yellowish-brown needles, melts at 59—60° and does not yield an osazone by atmospheric oxidation in an alcoholic solution of potassium hydroxide.

2 : 4 : 6-*Tribromo-3-hydroxybenzaldehydephenylhydrazone*, obtained in yellowish-brown crystals melting at 129°, yields a *diacetyl* derivative separating from glacial acetic acid in yellow crystals and melting at 107—110°. Oxidation experiments made on the preceding phenylhydrazone and on the corresponding derivative of tetrachloro-*m*-hydroxybenzaldehyde do not lead to the formation of osazones.

G. T. M.

Formation of Acetals from Hydroxynitriles. By ROBERT STOLLÉ (*Ber.*, 1902, **35**, 1590—1591).—On attempting to free freshly prepared mandelonitrile from water by filtration, it was converted into the *compound* $CHPh(O·CHPh·CN)_2$, which crystallises from alcohol, melts at 196·5°, and is easily obtained by mixing benzaldehyde and mandelonitrile with alcohol containing 1 per cent. of hydrogen chloride. The similar *compound*, $C_{26}H_{24}O_2N_2$, obtained from tolualdehydecyanohydrin, melts at 178°, whilst the *compound* $C_{24}H_{20}O_3N_2$, prepared from benzylidene cyanohydrin and anisaldehyde, melts at 224°.

Incidentally it is stated that aldehydes yield somewhat unstable additive compounds with mercuric chloride; that obtained from benzaldehyde is a white, flocculent mass having the composition

$$C_6H_5·CHO,HgCl_2,$$

and is decomposed into its constituents by boiling water.

W. A. D.

Oxidation of *p*-Hydroxybenzaldehydephenylhydrazone and certain Derivatives to α-Diketoneosazones. By HEINRICH BILTZ and OTTO AMME (*Annalen*, 1902, **321**, 1—32. Compare Abstr., 1899, i, 502, 910).—The process for preparing the aromatic α-diketoneosazones by oxidising the corresponding phenylhydrazones in alcoholic solution with atmospheric oxygen does not succeed in the case of *p*-hydroxybenzaldehyde itself, although the reaction takes place quite readily with certain of its derivatives.

3 : 5 : 3′ : 5′-*Tetrabromo*-4 : 4′-*dihydroxybenzil-β-osazone*,

$$C_2(N·NHPh)_2(C_6H_2Br_2·OH)_2,$$

prepared by passing air through a dilute alcoholic potassium hydroxide solution of 3 : 5-dibromo-4-hydroxybenzaldehyde phenylhydrazone, crystallises from dilute alcohol in small, white leaflets melting at 206°. The reaction takes place at the ordinary summer temperature, but when the mixture is cooled to $-6°$ or $-10°$ the stereoisomeric *α-osazone* is produced; this is also obtained in small, white leaflets, but it melts at 144°; it is not converted into its isomeride by boiling with phenylhydrazine, nitrobenzene, or glacial acetic acid, although the transformation is effected by the agency of acetic anhydride, both oximes yielding the same *triacetate*, which crystallises in white prisms, melts at 274—275°, and gives rise to the β-osazone on hydrolysis. The *tetra-acetate* results from the action of boiling acetic anhydride on the α-osazone; it separates in yellowish-white leaflets, melts at 161—162°, and is not obtained either from the β-osazone or the triacetate. The salicylosazones behave in a somewhat different manner on acetylation; when boiled for a short time with acetic anhydride, both stereoisomerides yield the same triacetyl derivative, which is triacetylsalicyl β-osazone, because it gives the β-osazone on hydrolysis; if, however, these osazones are heated with the anhydride in presence of sodium acetate, they both furnish the same tetra-acetate.

An oxidation of 3 : 5-dibromo-4-hydroxybenzaldehydephenylhydrazone with a definite volume of oxygen, either pure or atmospheric, showed that the reaction takes place quantitatively as follows:

$$2OH·C_6H_2Br_2·CH{:}N·NHPh + O_2 = H_2O_2 + C_2(N·NHPh)_2(C_6H_2Br_2·OH)_2$$

theoretical yields are only obtained, however, when dilute alcohol is employed as solvent, pure water or absolute alcohol giving less satisfactory results.

3 : 5 : 3′ : 5′-*Tetraiodo*-4 : 4′-*dihydroxybenzil-β-osazone*, obtained from 3 : 5-di-iodo-4-hydroxybenzaldehydephenylhydrazone (m. p. 157°) by the general method, crystallises from dilute alcohol in yellow leaflets and decomposes at 195°; the reaction takes place quantitatively in the manner indicated. The stereoisomeric *a-osazone* is produced when the experiment is performed at −5°; it crystallises from dilute alcohol with some difficulty and melts at 140—141°. The *triacetate* of the β-osazone represents the final product of the acetylation of this osazone, whereas the tetra-acetate is produced in any circumstance from the stereoisomeride; the former derivative crystallises in white leaflets melting at 270°, and the latter in yellow leaflets melting at 200°; both acetyl compounds yield the β-osazone on hydrolysis.

3 : 3′-*Dibromo*-4 : 4′-*dihydroxybenzilosazone*, produced from 3-bromo-4-hydroxybenzaldehydephenylhydrazone (m. p. 105°), melts at 120° whilst still impure, and yields tarry products on treatment with the ordinary solvents; its *triacetate* crystallises in white, flexible, felted needles and melts at 164°.

Vanillil-a-osazone, $C_2[C_6H_3(OH)\cdot OMe]_2(N_2HPh)_2$, prepared by oxidising vanillinphenylhydrazone at −11° to −15°, is a yellow powder consisting of small leaflets melting at 155°; this substance is not transformed into the β-isomeride either by heating its solutions or by acetylation.

3 : 3′-*Dinitro*-4 : 4′-*dihydroxybenzilosazone*, melting at 211°, is obtained by oxidising 3-nitro-4-hydroxybenzaldehydephenylhydrazone (m. p. 175°) at the ordinary temperature, and crystallises from nitrobenzene in rosettes of red prisms or lamellæ. When dissolved in alkali hydroxide solution and reprecipitated by acids, it becomes transformed into an *isomeride* melting at 130°; this substance, which is also formed as a direct product of oxidation, separates as a brownish-red, microcrystalline powder, and is reconverted into the osazone of higher melting point by warming or agitating with glacial acetic acid. A third stereoisomeric *osazone* melting at 245° is obtained in certain cases, but the conditions which determine its formation have not been precisely defined; it separates from nitrobenzene in small, red crystals, and it forms a soluble potassium derivative from the solutions of which it is reprecipitated by the addition of acids. In this case, the oxidation of the hydrazone does not take place at −10°.

On acetylation, the osazone melting at 211° yields a *tetra-acetate* which gives rise to the osazone melting at 130° on alkaline hydrolysis; the latter isomeride merely furnishes a *triacetyl* derivative even by the action of acetic anhydride and sodium acetate, this product when hydrolysed regenerating the original osazone. The tetra- and tri-acetyl derivatives separate from the ordinary organic solvents in yellowish-brown crystals and melt respectively at 239° and 248°. The third osazone yields an acetyl compound melting at 305°. G. T. M.

Derivatives of 2-Methyl*cyclo*hexanone. By Léon Tétry (*Bull. Soc. Chim.*, 1902, [iii], **27**, 302—307).—In the preparation of benzylidene-2-methyl*cyclo*hexanone (compare Wallach, Abstr., 1896, i, 572), the author has succeeded in isolating a new substance which crystallises in long, colourless needles melting at 152—153°, and is probably 1-*a-hydroxybenzyl-4-methyl*cyclo*hexanol*-2; it yields a *diacetate* which crystallises in colourless needles soluble in ether or light petroleum, and melts at 69—70°.

By the oxidation of benzylidenemethyl*cyclo*hexanone with permanganate, benzoic and β-methyladipic acids are obtained, and by reduction with sodium amalgam, *benzylmethyl*cyclo*hexanone*, a mobile, colourless oil boiling at 164° under 11 mm. pressure. The latter substance yields an *oxime* which crystallises in slender, silky needles, melts at 143°, and is very soluble in ether, benzene, or alcohol, but less so in light petroleum.

By the reduction of dibenzylidene-2-methyl*cyclo*hexanone with sodium amalgam, the corresponding *dibenzylmethyl*cyclo*hexanone* is obtained; it forms colourless needles which melt at 100° and are soluble in ether or alcohol. Neither the dibenzylidene nor the dibenzyl compound reacts with hydroxylamine. A. F.

3 : 5-Dinitroacetophenone and its Derivatives. By LUDWIG BEREND and FRITZ HEYMANN (*J. pr. Chem.*, 1902, [ii], **65**, 290—294).—3 : 5-*Dinitrobenzoyl chloride* crystallises from benzene in small, white needles, melts at 74°, and when treated with sodium and ethyl acetoacetate yields *ethyl* 3 : 5-*dinitrobenzoylacetoacetate*, which crystallises from alcohol in slender, bright yellow needles, or from ethyl acetate and light petroleum in long, compact prisms, and melts at 92°. The latter compound, when heated with 40 per cent. sulphuric acid for 8—10 hours, yields 3 : 5-*dinitroacetophenone*, which crystallises from light petroleum in lustrous needles, melts at 82—84°, and forms a *phenylhydrazone* melting at 212°. 3 : 5-*Diaminoacetophenone* crystallises from alcohol in bright yellow leaflets and melts at 133—134°.

3 : 5-*Dinitrobenzoylacetylacetone*, obtained from acetylacetone in a similar manner, crystallises from alcohol in lustrous, yellowish needles and melts at 153°. R. H. P.

Homologues of Deoxybenzoin. By MARYA STRZELECKA (*Bull. Acad. Sci. Cracow*, 1902, 12—13).—Phenyl *p*-xylyl ketone,

$$COPh\cdot CH_2\cdot C_6H_4Me,$$

is formed when a mixture of the barium salts of *p*-tolylacetic and benzoic acids is distilled under 60 mm. pressure; it melts at 57°, whilst Strassmann (Abstr., 1889, i, 883) gives 94°. The *oxime* crystallises in slender needles melting at 109°.

With alcoholic potassium thiocyanate, *p*-xylyl bromide gives *p-xylylthiocarbimide*, which crystallises in white needles melting at 134°.

K. J. P. O.

Synthesis of Hydroxyflavonole Derivatives. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1902, **35**, 1679—1683).—By condensing phenoxyacetophenone, $COPh\cdot CH_2\cdot OPh$, with metallic sodium, a *compound*, $C_{16}H_{12}O_2$, is obtained, which crystallises from alcohol in orange-coloured needles melting at 120°, and on reduction yields a substance crystallising from alcohol in white needles melting at 118°.

The *phenylhydrazone* of 2 : 4 : 6-trimethoxydiphenyltriketone,

$$C_6H_2(OMe)_3\cdot CO\cdot CBz{:}N\cdot NHPh,$$

results from the action of benzenediazonium chloride on benzoyl-2 : 4 : 6-trimethoxyacetophenone, and crystallises from alcohol in plates melting at 137°. The *phenylhydrazones* of 2 : 4 : 6 : 4′-tetramethoxybenzoylacetophenone and 2 : 4 : 6 : 3′-tetramethoxy-4′-ethoxybenzoylacetophenone crystallise in leaflets melting respectively at 169° and 166—167°. These three phenylhydrazones dissolve in concentrated sulphuric acid to deep red solutions.

The *phenylhydrazone* of 2 : 4 : 6-trimethoxy-2′-ethoxybenzoylacetophenone forms orange-yellow needles and melts at 88—90°. G. T. M.

β-Ionone. Haarmann & Reimer (D.R.-P. 126959. Compare this vol., i, 342).—*β-Ionone* is readily obtained by heating *cyclo*citralideneacetoacetic acid (β-iononecarboxylic acid) at 220° in a current of carbon dioxide, distilling the residue in steam, and fractionating the oily distillate under diminished pressure, the fraction boiling at 135—145° being utilised as a source of the ketone. G. T. M.

Acetylionone. Haarmann & Reimer (D.R.-P. 126960. Compare preceding abstract).—Acetyl-ψ-ionone (compare this vol., i, 342, 385), when heated under diminished pressure, becomes transformed into an isomeride melting at 121—122°, this product being of little use in the production of acetylionone. When, however, acetyl-ψ-ionone is treated at −10° with 80 per cent. sulphuric acid and the mixture subsequently heated at 50°, it undergoes transformation into *acetylionone*; this substance, which is obtained by diluting the product and distilling in steam, is a yellow oil, having an agreeable odour, boiling at 170—177° under 25 mm. pressure, and having a sp. gr. 1·03, and n_D 1·521 at 18°. Ionone is produced from the acetyl derivative by hydrolysis with alkalis. G. T. M.

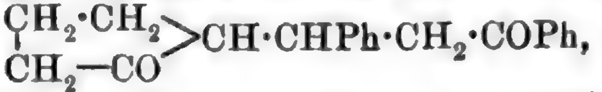
Homologues of Ionone. Haarmann & Reimer (D.R.-P. 127424).—Citral and the homologues of acetone, when condensed with concentrated acids at low temperatures, furnish homologues of ionone, sulphuric acid giving rise to β-substituted ionones, whilst phosphoric or formic acid generally induces the formation of the corresponding α-derivatives.

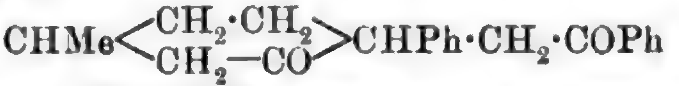
β-Methylionone, obtained from citral and methyl ethyl ketone and 70 to 100 per cent. sulphuric acid at 0°, boils at 140—155° under 20 mm. pressure, and has a sp. gr. 0·935—0·938 at 20°; *α-methylionone*, produced by the aid of phosphoric acid at 30°, boils at 140—150° under 20 mm. pressure and has a sp. gr. 0·925—0·931 at 20°.

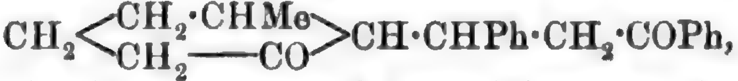
β-Dimethylionone, prepared from citral and methyl *iso*propyl ketone, boils at 155—160° under 20 mm. pressure, whilst the α-derivative boils at 150—155° under the same pressure. G. T. M.

Separation of Ianthone from Ionone. Haarman & Reimer (D.R.-P. 127831).—Crude ianthone is treated with a slightly acid solution of sodium phenylhydrazine-*p*-sulphonate, the mixture being subsequently rendered alkaline with sodium hydroxide and extracted with ether. Under these conditions, the ionone condenses with the hydrazine derivative to form a hydrazone soluble in sodium hydroxide, whilst the ianthone, which is not affected, is removed by the ether, and finally purified by distillation under diminished pressure. Ianthone is a pale yellow oil boiling at 162—172° under 15 mm. pressure and having a sp. gr. 0·943 and n_D 1·5376 at 22°.

G. T. M.

Semi-cyclic 1 : 5-Diketones. By HANS STOBBE (*Ber.*, 1902, **35**, 1445—1448).—The *diketone*,  $\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{-}CO\end{array}\!\!>\!CH{\cdot}CHPh{\cdot}CH_2{\cdot}COPh$, prepared from *cyclo*pentanone and benzylideneacetophenone, crystallises from light petroleum in small prisms and melts at 78—80°. The *semicarbazone*, $C_{22}H_{26}O_2N_6$, is insoluble in most solvents and melts and decomposes at 233°.

The *diketone*,  $CHMe\!<\!\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{-}CO\end{array}\!\!>\!CHPh{\cdot}CH_2{\cdot}COPh$ or



$$CH_2\!<\!\begin{array}{l}CH_2{\cdot}CHMe\\ CH_2{-\!-}CO\end{array}\!\!>\!CH{\cdot}CHPh{\cdot}CH_2{\cdot}COPh,$$

from β-methyl*cyclo*hexanone and benzylideneacetophenone, crystallises from alcohol and melts at 149—151°. The *monoxime*, $C_{22}H_{25}NO_2$, crystallises from alcohol or benzene and melts at 215—216°.

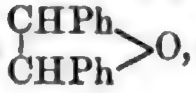
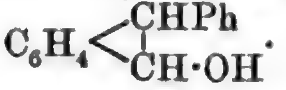
T. M. L.

Intramolecular Atomic Migrations. I and II. By P. J. MONTAGNE (*Rec. Trav. Chim.*, 1902, [ii], **21**, 6—29, 30—37).—I. The conversion of aromatic α-diketones under the influence of alkalis into acids, as instanced in the change of benzil, COPh·COPh, into benzilic acid, $OH{\cdot}CPh_2{\cdot}CO_2H$, has been studied with the object of determining whether the carbon atom of the wandering benzene nucleus, to which is attached the carbonyl group in benzil, also unites the phenyl group to the α-carbon atom in benzilic acid. With alkalis, 4 : 4′-dichlorobenzil yields a dichlorobenzilic acid, which is oxidised to a 4 : ?′-dichlorobenzophenone ; in the latter, the position of only one of the chlorine atoms is fixed. The following facts show that this substance is 4 : 4′-dichlorobenzophenone, and that the carbon atom which is linked to the carbonyl group in benzil is also attached to the α-carbon atom in benzilic acid. The dichlorobenzophenone, on nitration, yields a dinitro-derivative identical with that obtained from the 4 : ?′-dichloro-3-nitrobenzophenone prepared from 4-chloro-3-nitrobenzoyl chloride and chlorobenzene ; on reducing the mononitro-derivative, the corresponding 4 : ?′-dichloro-3-aminobenzophenone is formed, which, when oxidised, yields *p*-chlorobenzoic acid, the nucleus containing the amino-group being broken up. Thus the second chlorine atom in the dichlorobenzophenone, obtained from dichlorobenzilic acid, must be in the para-position relatively to the carbonyl group.

4 : 4′-*Dichlorohydrobenzoin*, $C_2H_2(C_6H_4Cl)_2(OH)_2$, prepared by reducing *p*-chlorobenzaldehyde with zinc and hydrochloric acid, crystallises in small, colourless needles melting at 151°, and on oxidation with dilute nitric acid gives 4 : 4′-*dichlorobenzil*, which crystallises in

long, yellow needles melting at 200°. 4 : 4′-*Dichlorobenzilic acid*, $OH\cdot C(C_6H_4Cl)_2\cdot CO_2H$, prepared from 4 : 4′-dichlorobenzil by the action of alcoholic potassium hydroxide, forms slender needles melting at 101·75° and dissolves in sulphuric acid with a red coloration; the *silver* salt crystallises from benzene with $1C_6H_6$ in colourless needles; the *methyl* ester forms white needles melting at 60°, and decomposes on heating into 4 : 4′-dichlorobenzophenone, carbon monoxide, and methyl alcohol. On oxidising dichlorobenzilic acid with chromic acid, 4 : 4′-dichlorobenzophenone (m. p. 147·75° and b. p. 353° at 757 mm. pressure) was obtained (Dittrich, Abstr., 1891, i, 1237). 4 : 4′-*Dichloro-3-nitrobenzophenone,* $NO_2\cdot C_6H_3Cl\cdot CO\cdot C_6H_4Cl$, prepared from 4-chloro-3-nitrobenzoyl chloride and chlorobenzene in the presence of aluminium chloride, crystallises in colourless needles melting at 87°. On nitrating dichlorobenzophenone or dichloronitrobenzophenone, 4 : 4′-*dichlorodinitrobenzophenone* is formed and melts at 132·5°. On reducing the mononitro-derivative with stannous chloride, 4 : 4′-*dichloro-3-aminobenzophenone* is obtained, crystallising in yellow needles melting at 140·5° and boiling at 280° under 11 mm. pressure; when oxidised by permanganate, *p*-chlorobenzoic acid is formed, and by the action of nitrous acid 4 : 4′-dichlorobenzophenone is produced.

II. With the same object as that stated in the preceding section, the transformation of 4 : 4′-dichlorohydrobenzoin (an aromatic α-glycol) into 4 : 4′-dichlorophenylacetaldehyde has been studied. The transformation is effected by heating the α-glycol with excess of 35 per cent. sulphuric acid under pressure at 150—160° for 36 hours; 4 : 4′-*dichlorodiphenylacetaldehyde*, $CH(C_6H_4Cl)_2\cdot CHO$, thus obtained, forms crystals melting at 149°, and is oxidised by chromic acid to 4 : 4′-dichlorobenzophenone (*loc. cit.*).

The intermediate product, $C_{14}H_{12}O$, obtained in the transformation of hydrobenzoin into diphenylacetaldehyde, must, in consequence, have the formula  $\left.\begin{matrix}\mathrm{CHPh}\\|\\\mathrm{CHPh}\end{matrix}\right>O$, and not  $C_6H_4<\begin{matrix}\mathrm{CHPh}\\|\\\mathrm{CH\cdot OH}\end{matrix}$. K. J. P. O.

Reactions of the Dihalogen-thymoquinones. By O Böters (*Ber.*, 1902, **35**, 1502—1510. Compare Hoffmann, Abstr., 1901, i, 473).—The condensation between dibromothymoquinone and aniline or *p*-toluidine, involving the replacement of the methyl radicle by the arylamino-residue, takes place in a similar manner with *m*-toluidine and anisidine; dichlorothymoquinone is found to react in the same way.

3 : 6-*Dibromo*-5-m-*toluidino*-2-iso*propylbenzoquinone,*

$C_6Pr^{\beta}Br_2O_2\cdot NH\cdot C_6H_4Me$,

crystallises from methyl alcohol in violet leaflets melting at 171°; it is sparingly soluble in alcohol or benzene, dissolving more readily in acetone.

3 : 6-*Dibromo-5-anisidino*-2-iso*propylbenzoquinone,*

$C_6Pr^{\beta}Br_2O_2\cdot NH\cdot C_6H_4\cdot OMe$,

separates from alcohol in deep blue or violet needles which melt at 196° The solution of these derivatives in concentrated sulphuric acid has a deep blue colour, and the compounds, when boiled with alcoholic sulphuric acid, are hydrolysed into 3 : 6-dibromo-5-hydroxy-2-*iso*propylbenzoquinone, which combines with *p*-toluidine in methyl alcohol solution to yield the corresponding *salt*, $C_6Pr^{\beta}Br_2O_2\cdot OH,C_6H_4Me\cdot NH_2$, a substance separating in brick-red needles melting at 150°.

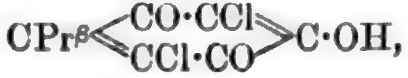
The *xylidine* salt, $C_6Pr^{\beta}Br_2O_2\cdot OH,C_6H_3Me_2\cdot NH_2$, prepared in a similar manner, forms slender, deep violet needles melting at 154°.

3 : 6-*Dichloro*-5-p-*toluidino*-2-iso*propylbenzoquinone*,

$$C_6Pr^{\beta}Cl_2O_2\cdot NH\cdot C_6H_4Me,$$

produced by boiling together dichlorothymoquinone and *p*-toluidine in alcoholic solution, separates in deep violet leaflets and melts at 187°; it is easily soluble in benzene, and only sparingly so in alcohol; its solution in concentrated sulphuric acid has a fine blue colour.

3 : 6-*Dichloro*-5-*hydroxy*-1-iso*propylbenzoquinone*,



$$CPr^{\beta}<\begin{matrix}CO\cdot CCl\\ CCl\cdot CO\end{matrix}>C\cdot OH,$$

obtained by boiling the preceding substance with alcoholic hydrogen chloride, separates from the cold solution in golden-yellow needles with a bronze reflex; it melts at 126° and is readily soluble in alcohol and solutions of the alkali hydroxides, carbonates, or hydrogen carbonates. The *silver* salt crystallises from dilute alcohol in white needles. The *methoxy*-derivative, $C_6Pr^{\beta}Cl_2O_2\cdot OMe$, formed by the action of methyl iodide on the silver salt, crystallises from dilute alcohol in golden-yellow leaflets and melts at 83—84°.

The position of the substituent radicles in the basic molecule has an appreciable influence on the course of these condensations, for *o*-toluidine and *p*-xylidine, which contain a methyl group in the ortho-position with respect to amidogen, give rise to diaminoquinones, the methyl group and one of the bromine atoms of dibromothymoquinone being simultaneously eliminated.

6-*Bromo*-3 : 5-*di*-o-*toluidino*-1-iso*propylbenzoquinone*,

$$C_6Pr^{\beta}BrO_2(NH\cdot C_6H_4Me)_2,$$

which is obtained only in small yield, crystallises from alcohol in deep violet leaflets melting at 131°.

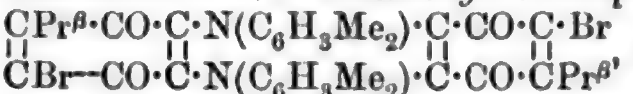
6-*Bromo*-3 : 5-*di*-p-*xylidino*-1-iso*propylbenzoquinone*,

$$C_6Pr^{\beta}BrO_2(NH\cdot C_6H_3Me_2)_2,$$

crystallises from alcohol in reddish-brown needles with a coppery lustre; it melts at 166° and dissolves in concentrated sulphuric acid to a brownish-violet solution.

When boiled with alcoholic sulphuric acid or hydrogen chloride, this compound undergoes a condensation whereby two mols. coalesce to form a substituted phenazine, two mols. of *p*-xylidine being simultaneously eliminated. This reaction serves to establish the orientation of the radicles in the dixylidinoquinone itself.

4 : 9-*Dibromo*-2 : 5 : 7 : 10-*tetraoxy*-1 : 6-*di*-p-*xylyl*-3 : 8-*di*iso*propylphenazine*,



$$\begin{array}{l}CPr^{\beta}\cdot CO\cdot C\cdot N(C_6H_3Me_2)\cdot C\cdot CO\cdot C\cdot Br\\ \,\| \qquad\qquad\;\, \| \qquad\qquad\qquad\quad\;\; \| \qquad\quad\;\; \|\\ CBr—CO\cdot C\cdot N(C_6H_3Me_2)\cdot C\cdot CO\cdot CPr^{\beta}\end{array},$$

crystallises from absolute alcohol in yellow needles melting at 215°; its solution in concentrated sulphuric acid has a yellowish-brown colour. This substance is also produced by the action of alcoholic hydrogen bromide, but when hydrogen chloride is employed, the corresponding *dichlorophenazine* derivative is obtained; this compound, which has the same configuration as the preceding phenazine, contains the two chlorine atoms in the positions

4 and 9; it crystallises from a mixture of benzene and light petroleum in greenish-yellow needles melting at 236°.

The aliphatic amines behave differently towards dibromothymoquinone, this substance, when boiled with a methyl alcohol solution of methylamine, losing both its halogen radicles and becoming converted into 3:6-*dimethylaminothymoquinone*, $C_6MePr^{\beta}O_2(NHMe)_2$, a compound crystallising in reddish-violet needles or plates melting at 203°, and dissolving in concentrated sulphuric acid to a yellow solution.

G. T. M.

Dyeing with Mordants. By CARL LIEBERMANN (*Ber.*, 1902, **35**, 1490—1498).—Remarks suggested by a discourse delivered by Noelting on the theory of dyeing colouring matters on basic mordants.

The rule put forward by the author and Kostanecki, to connect the dyeing properties of hydroxyanthraquinone derivatives with their configuration, still applies generally to the other colouring matters of this type which have been subsequently discovered. According to this generalisation, the property of giving valuable colour lakes with the basic oxide mordants depends on the presence in the molecule of two hydroxyl groups or one carboxyl and one hydroxyl radicle in ortho-positions with respect to each other when one of the substituents is adjacent to the chromophoric residue.

The azo-compounds derived from diazotised anthranilic acid coupled with resorcinol and β-naphthol which dye wool mordanted with the basic oxides, probably owe this property to the presence of the carboxyl and hydroxyl radicles situated in ortho-positions with respect to the azo-group as indicated by the formulæ $CO_2H\cdot C_6H_4\cdot N{:}N\cdot C_6H_3(OH)_2$ and $CO_2H\cdot C_6H_4\cdot N{:}N\cdot C_{10}H_6\cdot OH$. Consequently these substances may be considered to follow the rule.

The author now divides colouring matters of this type into two classes. Firstly, those which rapidly give deep shades of colour with the ordinary mordanting oxides (aluminic and ferric oxides), and, secondly, the compounds which either do not dye with the ordinary basic mordants or at least only give very faint tints. The substances belonging to the second class may, however, give very good results with the oxides of the rarer metals.

The *o*-dihydroxy-compounds belong to the first class, whilst those derivatives containing the substituent radicles in other positions belong to the second. Anthrachrysone (1:3:5:7-tetrahydroxyanthraquinone) belongs to the second class, whilst hystazarin (2:3-dihydroxyanthraquinone) and quinizarin (*p*-dihydroxyanthraquinone) occupy an intermediate position, for even when carefully purified they produce moderately deep shades of colour on fabrics mordanted with ferric oxide or alumina. These three anthraquinone derivatives, however, all give better results with the rare oxides.

G. T. M.

Conversion of Nitroanthraquinone Derivatives into Substituted Bromoaminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 128845).—1-Nitroanthraquinone and 1:8-dinitroanthraquinone, when heated at 150° with bromine and glacial acetic acid, become converted into *dibromo*-1-*aminoanthraquinone* and tetrabromo-1 : 8-diaminoanthraquinone respectively; these products are dark red powders insoluble in water, but soluble in alcohol, glacial acetic acid, xylene, nitrobenzene, or aniline to orange-coloured solutions.

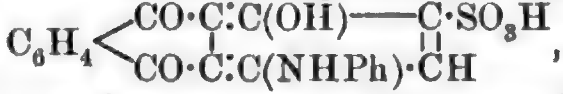
Dibromo-β-aminoanthraquinonesulphonic acid, prepared by heating β-nitroanthraquinonesulphonic acid with concentrated hydrobromic acid, dissolves in water to an orange-coloured solution.

The properties of these compounds are tabulated. G. T. M.

Derivatives of Nitroaminoanthraquinone. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127780).—*Diacetyl*-1 : 5-*diaminoanthraquinone*, produced by acetylating 1 : 5-diaminoanthraquinone with acetic anhydride, separates in light brown, lustrous crystals, melts above 300°, and is converted into 4 : 8-*dinitrodiacetyl*-1 : 5-*diaminoanthraquinone* by the action of a mixture of concentrated nitric and sulphuric acids. The product is a yellow, crystalline powder, very sparingly soluble in the ordinary solvents but crystallising from benzene in brownish-yellow prisms. 4 : 8-*Dinitro*-1 : 5-*diaminoanthraquinone*, obtained in the form of its colourless *sulphate* by the action of concentrated sulphuric acid at 90° on the acetyl compound, crystallises from nitrobenzene in dark red leaflets with a green reflex; the sulphate crystallises in flattened prisms.

4 : 5-*Dinitrodiacetyl*-1 : 8-*diaminoanthraquinone*, prepared in a similar manner to its isomeride, is a yellow, crystalline powder. When hydrolysed, it yields 4 : 5-*dinitro*-1 : 8-*diaminoanthraquinone*, a substance separating from pyridine or nitrobenzene in yellow crystals and giving rise to 1 : 4 : 5 : 8-tetra-aminoanthraquinone on reduction with sodium stannite. G. T. M.

Dihalogen Derivatives of 1 : 5-Diaminoanthraquinonedisulphonic Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126393).—*Sodium dichloro*-1 : 5-*diaminoanthraquinonedisulphonate*, produced by adding sodium chlorate to a warm solution of sodium 1 : 5-diaminoanthraquinonedisulphonate in dilute sulphuric acid, separates from the mixture in yellowish-red needles on adding sodium chloride or hydroxide; it dyes unmordanted wool in scarlet shades. The corresponding *dibromo-sulphonate* is obtained in a similar manner by substituting bromine dissolved in glacial acetic acid or dilute hydrochloric acid for the chlorate; it crystallises from water in slender needles insoluble in the organic solvents. G. T. M.

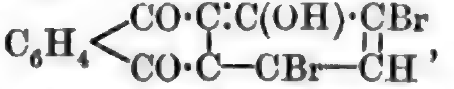
Introduction of Amino-radicles into 4-Nitro-1-hydroxyanthraquinone-2-sulphonic Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127438).—4-p-*Toluidino*-1-*hydroxyanthraquinone*-2-*sulphonic acid*,  $C_6H_4{<}\begin{matrix}CO\cdot \underset{|}{C}{:}C(OH)\text{——}\underset{||}{C}\cdot SO_3H\\ CO\cdot C{:}C(NHPh)\cdot CH\end{matrix}$, obtained by heating 4-nitro-1-hydroxyanthraquinone-2-sulphonic acid with *p*-toluidine in 50 per cent. acetic acid, is sparingly soluble in water, dissolving either in this solvent or in alcohol to a blue solution. The corresponding *phenyl* and *a-naphthyl* compounds have similar properties; they dissolve in concentrated sulphuric acid to yellow solutions, the addition of boric acid developing a green coloration. G. T. M.

Bromo-β-aminoalizarin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 126603).—β-Aminoalizarin cannot be brominated by bromine dissolved in glacial acetic or concentrated sulphuric acid, but *bromo-β-aminoalizarin* is obtained when the reagent dissolved in a mixture of the two solvents is allowed to act at 150°. The product crystallises from glacial acetic acid in brown needles melting at 287°.

G. T. M.

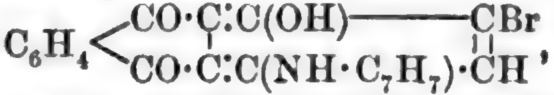
[Quinizarin Derivatives.] FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127532).—The halogen derivatives of quinizarin containing a halogen atom in the 2-position exchange this radicle for the residue R·NH– when heated with aromatic amines.

2 : 4-*Dibromo-1-hydroxyerythroanthraquinone*,



$$C_6H_4<\begin{array}{l}CO\cdot C:C(OH)\cdot CBr \\ CO\cdot C—CBr—CH\end{array},$$

prepared by heating sodium hydroxyerythroanthraquinonesulphonate with bromine and water at 120—130°, crystallises in reddish-yellow needles and melts at 233°. When heated with *p*-toluidine at 80—100°, this substance loses the bromine atom in the 4-position and becomes converted into the *bromoquinizarin-blue*,



$$C_6H_4<\begin{array}{l}CO\cdot C:C(OH)——CBr \\ CO\cdot C:C(NH\cdot C_7H_7)\cdot CH\end{array},$$

which crystallises in blue needles developing a green coloration with concentrated sulphuric acid.

G. T. M.

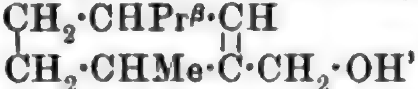
***p*-Halogen Derivatives of Hydroxyanthraquinones.** FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127699. Compare preceding abstract).—p-*Dichloroanthrarufin*, prepared by passing chlorine into a glacial acetic acid solution of anthrarufin, separates in red needles having a metallic lustre; it is very sparingly soluble in solvents of low boiling point, but dissolves in nitrobenzene, separating in crystals having a red metallic lustre; its solution in a mixture of boric and sulphuric acids has a characteristic spectrum.

p-*Dichlorochrysazin*, produced either by direct chlorination in glacial acetic acid solution or by treatment with sodium chlorate and hydrochloric acid in a hot aqueous suspension, separates from nitrobenzene in crystals having a metallic lustre.

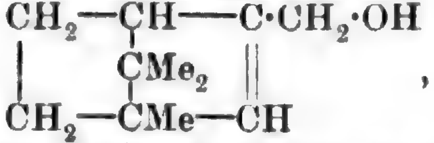
p-*Dibromoanthrarufin* is obtained by the action of potassium bromate and hydrobromic acid on a glacial acetic acid solution of anthrarufin; p-*dibromochrysazin* is prepared in a similar manner

G. T. M.

Monohydric Cyclic Alcohols. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 127855. Compare this vol., i, 102 and 299).—The cyclic glycols of the terpene series, when heated either alone or with dehydrating agents, yield unsaturated monohydric alcohols.

Dehydromenthylcarbinol,  $\begin{array}{l}CH_2\cdot CHPr^{\beta}\cdot CH \\ CH_2\cdot CHMe\cdot C\cdot CH_2\cdot OH\end{array}$, distils from a boiling mixture of *cis*-menthylglycol and 20 per cent. sulphuric acid as a limpid, highly refractive oil having an odour of anise; it boils at 99—101° under 18 mm. pressure. *Menthylcarbinol* is obtained on reducing the preceding compound with sodium and absolute alcohol; it is a colourless oil boiling at 85—90° under 20 mm. pressure.

Dehydrocamphylcarbinol (*camphenylcarbinol*),



is prepared by saturating the fused mixture of *cis*- and *trans*-camphanylglycols or their solution in benzene with hydrogen chloride, the product being rendered alkaline with sodium hydroxide and distilled in steam; the carbinol distils over, whilst the unaltered *trans*-camphanylglycol remains in the residue. The carbinol solidifies to a mass of colourless needles; it boils at 128—129° under 19 mm. pressure and has the odour of vanillin. *Camphanylcarbinol* results from the reduction of the preceding compound; it crystallises in colourless needles and melts at 62—64°. G. T. M.

Syntheses in the Hydroaromatic Series by the Action of Zinc Chloride. By Iwan L. Kondakoff [and, in part, E. Lutschinin] (*J. pr. Chem.*, 1902, [ii], **65**, 201—233. See Abstr., 1900, i, 105).—A discussion of the formulæ of camphene, fenchene, fenchyl alcohol, &c., mainly polemical against G. Wagner.

The following new esters have been obtained by treating the corresponding hydrocarbon with a mixture of the acid and zinc chloride: iso*Bornyl* iso*butyrate*, which is a colourless, viscous oil, boils at 132—133° under 19 mm. pressure, has a sp. gr. 0·9628 at 20°/20° and n_D 1·46276, and is optically inactive. iso*Bornyl* iso*valerate*, which boils at 132—133° under 13 mm. pressure, has a sp. gr. 0·9523 at 20°/20°, n_D 1·46038, and $[\alpha]_D$ +47° (the *iso*valeric acid used had $[\alpha]_D$ +2°8′ at 20°). iso*Fenchyl* iso*valerate*, which boils at 142—145° under 19 mm. pressure, has a sp. gr. 0·9437 at 20°/20°, n_D 1·45749, and α_D −30′ (the fenchene had $[\alpha]_D$ +6°55′ and the *iso*valeric acid $[\alpha]_D$ 2°8′).

It is shown that commercial camphene and fenchene each contain two isomeric substances, one having the double linking in the side chain and the other in the ring. R. H. P.

The Resin of Dammara Orientalis (Manila Copal). By Alexander Tschirch and M. Koch (*Arch. Pharm.*, 1902, **240**, 202—229).—Two specimens of Manila copal were examined. The first was soluble in alcohol, comparatively soft, and with a dull surface. The resin melted at 115°; it had an acid number 134 determined by direct titration, 173 determined indirectly, saponification number 190, and iodine number 55·4. Succinic, formic, and acetic acids were detected amongst the products obtained by distilling the resin. Water extracted a minute quantity of a bitter substance. From a solution of the resin in ether, 1 per cent. aqueous ammonium carbonate extracted two acids. One of these, *mancopalic acid*, $C_8H_{12}O_2$, crystallised slowly from a solution of the two in a mixture of ethyl and methyl alcohols; it melts at 175° and has a specific rotation +56°, an acid and saponification number 397, corresponding with monobasicity, and an iodine number 90·5, corresponding with a monoiodo-derivative; the *potassium* and *silver* salts were analysed; the acid contains no methoxyl groups, and does not react with phenylhydrazine. The second acid, *mancopalenic acid*, $C_8H_{14}O_2$, present in larger quantity, is amorphous; it melts at 100—105°, has an acid and saponification number 394, corresponding with monobasicity, and an iodine number 90·9, corresponding with a monoiodo-derivative. From the remaining ethereal solution, 1 per cent. aqueous sodium carbonate extracted the closely related isomeric α- and *β-mancopalolic* acids, $C_{10}H_{18}O_2$, which only differ in that the former melts at 85—100° and forms a lead salt which is insoluble in alcohol, whilst the second melts at 83—88° and forms a lead salt soluble in alcohol. Both have the acid and saponification number 326, corresponding with monobasicity, and the iodine number 74·5, corresponding with a monoiodo-derivative. The residue, when freed from ether and distilled with steam, yielded as a distillate an *essential oil* boiling at 165—170° and having a sp. gr. 0·849 at 15°, whilst there remained behind *mancopaloresen*, $C_{20}H_{32}O$, which is amorphous, melts at 80—85°, and is indifferent to alkalis. In 100 parts of the drug there were contained: mancopalic and mancopalenic acids, 4; mancopalolic acids, 75; mancopaloresen, 12; essential oil, 6; water, 2; other substances, 1.

The second specimen of Manila copal was partially soluble in alcohol, comparatively hard, and with a shining surface. It melted at 120°, had an acid number 118 by direct titration, 157 determined indirectly, a saponification number 165, and an iodine number 55·0. It contained no acids that could be extracted by ammonium carbonate from the ethereal solution; in other respects, it resembled the first sample, yielding the same mancopalolic acids and mancopaloresen. In 100 parts there were contained: α- and β-mancopalolic acids, 80; essential oil, 5; mancopaloresen, 12; water, 2; other substances, 1.

The two samples appear to be derived from the same plant, and the results of the investigation confirm Wiesner's conclusion (*Rohstoffe des Pflanzenreiches*) that Manila copal is derived from one of the *Coniferæ*, *Dammara orientalis*, and not from *Vateria indica*, one of the *Dipterocarpeæ*.

C. F. B.

Constitution of Chitin. By SIGMUND FRÄNKEL and AGNES KELLY (*Monatsh.*, 1902, **23**, 123—132).—When chitin is treated with cold 70 per cent. sulphuric acid, the liquid gradually darkens and smells of acetone. After 2—3 days, the action is stopped by pouring into ice-water, and a series of decomposition products are obtained. Two of these have been investigated. *n*-Acetylglucosamine is easily soluble in water, with difficulty in methyl or ethyl alcohol, and insoluble in ether; it crystallises in long needles, melts with decomposition at about 190°, has a neutral reaction, and a strong reducing action on alkaline copper solutions; it does not form salts with acids, or a phenylhydrazine derivative. It has $[\alpha]_D$ +41·86°, and is identical with Breuer's acetylglucosamine (Abstr., 1898, i, 620). When boiled with sodium acetate and acetic anhydride, it does not form either of Lobry de Brun and Ekenstein's pentacetylglucosamines (Abstr., 1899, i, 732).

The authors consider the other decomposition product to be *monoacetyldiglucosamine*, $C_{14}H_{26}O_{10}N_2$. It is easily soluble in water, the solution being dextrorotatory, does not reduce alkaline copper solutions, and gives no reaction with iodine or precipitate with neutral or basic lead acetate solution. It is not identical with Araki's chitosan (Abstr., 1895, i, 444). The authors consider that the molecular formula of chitin is a multiple of $C_{18}H_{30}O_{12}N_2$. G. Y.

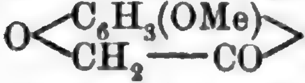
Ononin. By Franz von Hemmelmayr (*Monatsh.*, 1902, **23**, 133—164. Compare Abstr., 1901, i, 160).—By crystallisation from alcohol, crude ononin, obtained from the ononis root, is separated into three fractions. The least soluble of these contains onon and ononin. *Onon*, $C_{29}H_{33}O_{12}$, is very slightly soluble in boiling water, alcohol or benzene, easily so in boiling glacial acetic acid and in pyridine, melts with decomposition at 270°, and with concentrated sulphuric acid and manganese dioxide forms a bright red liquid. Boiling baryta water has has little action on it. When boiled with normal sulphuric acid, it yields an amorphous substance, which sinters at 210° and melts and decomposes at 250°, the filtrate reduces alkaline copper solutions, and with phenylhydrazine yields glucosazone.

Ononin is separated from onon by extraction with boiling water, from which it crystallises in colourless needles, which sinter at 204° and melt at 210°. With manganese dioxide and sulphuric acid, it forms a cherry-red, almost violet liquid. Heated with baryta water for 15 minutes, it yields onospin, prolonged heating giving ononetin. When heated at 100° with normal sulphuric acid, ononin yields dextrose, and Hlasiwetz's formylononetin, $C_{19}H_{14}O_5$, which is hydrolysed by baryta water to formic acid and ononetin. The ononetin obtained in this way shows the same behaviour as to its melting point as that from ononin and onospin, and consists of two isomerides. A methoxyl determination showed formylononetin to contain one methoxy-group. When boiled with acetic anhydride and sodium acetate, it yields a *monoacetyl* derivative, which is easily soluble in hot alcohol, chloroform or glacial acetic acid, and crystallises in stellate aggregates melting at 164—165°. Ebullioscopic molecular weight determinations gave 293, 279. $C_{21}H_{16}O_6$ requires 364.

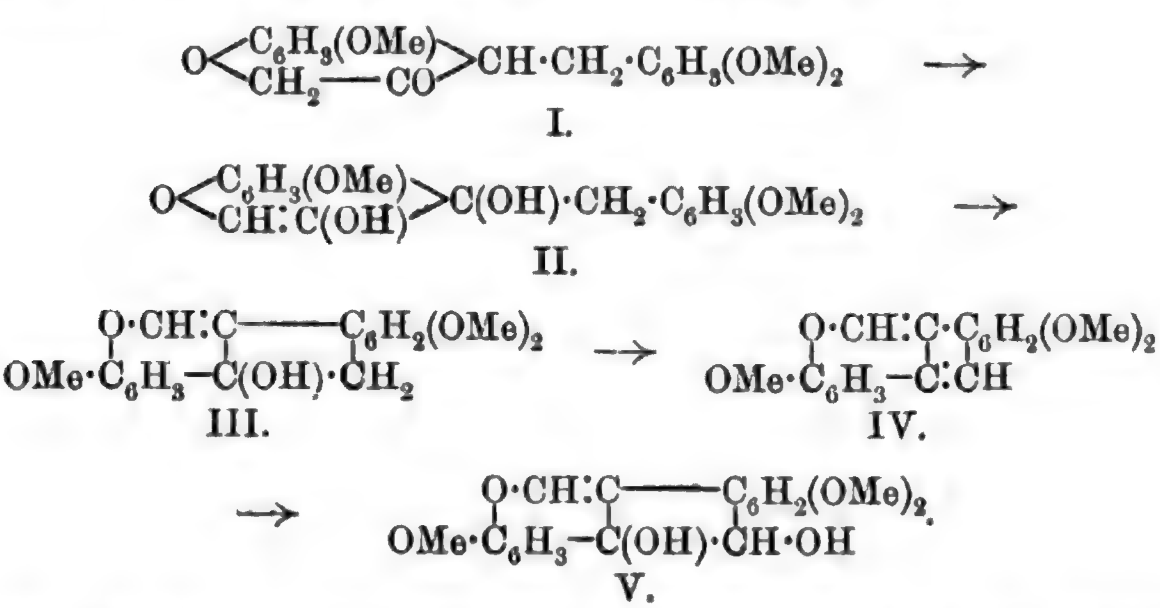
The author considers that the correct formula for ononin is $C_{25}H_{26}O_{11}$, for onospin, $C_{24}H_{26}O_{10}$, for ononetin, $C_{18}H_{16}O_5$.

The middle fraction from the crude ononin consists of ononin in small quantity, and ψ-ononin. The latter, separated by further fractional crystallisation from alcohol, forms a white, indistinctly crystalline mass, which melts at 206—207°, and gives a brown coloration with manganese dioxide and sulphuric acid. It is only moderately soluble in water or alcohol. When boiled with water, it is slowly converted, more quickly with baryta water, into *ψ-onospin*, $C_{24}H_{24}O_{11}$, which is easily soluble in hot water. From much water, it separates in a matted mass of delicate white needles, which contain $2\frac{1}{2}H_2O$, and melt at 220—221°. From a concentrated aqueous solution, it separates in similar crystals, which melt at 195—197°, and contain only a small percentage of water. Molecular weight determinations gave for the crystals of higher melting point 536, for those of lower melting point 518; $C_{24}H_{24}O_{11}$ requires 488.

When boiled with dilute sulphuric acid, ψ-onospin is hydrolysed to dextrose and an amorphous substance. With acetic anhydride and sodium acetate, it forms a *tetra-acetyl* derivative, which melts at 188—189°. With butyric anhydride and sodium butyrate, it forms a *tetrabutyryl* derivative melting at 116°. From the most soluble fraction from the crude ononin, there have been separated a glucoside melting at 120—130°, and three substances melting respectively at about 100°, 220—230° and 125—130°. G. Y.

Brazilin. By STANISLAUS VON KOSTANECKI and V. LAMPE (*Ber.*, 1902, **35**, 1667—1674. Compare Abstr., 1899, i, 538, and Gilbody, Perkin, and Yates, Trans., 1901, **79**, 1396).—The formula for trimethylbrazilin suggested by Feuerstein and Kostanecki readily accounts for the formation of 2-carboxy 5-methoxyphenoxyacetic acid on oxidation, providing that it is written in its tautomeric form,  $O<\begin{array}{l}C_6H_3(OMe)\\CH_2—CO\end{array}>CH\cdot CH_2\cdot C_6H_3(OMe)_2$. This ether, which is readily obtained by methylating brazilin with methyl sulphate in a boiling solution of potassium hydroxide, yields the crystalline acetyl derivative melting at 174—176° when heated with acetic anhydride. The trimethyl ether on oxidation with cold chromic acid, yields a substance, $C_{19}H_{16}O_6$, separating from alcohol or benzene in colourless, acicular crystals decomposing at 165°. In spite of the difference in properties, this product is considered to be identical with trimethylbrazilone described by Gilbody and Perkin as crystallising in yellow needles and melting at 191°. The acetyl derivative of trimethylbrazilin on oxidation with cold chromic acid yields a compound, $C_{19}H_{16}O_6$, recently described by Herzig and Pollok as β-trimethylbrazilone (compare this vol., i, 483).

The trimethylbrazilone, obtained from trimethylbrazilin, behaves like a glycol rather than a ketone, and when heated above its melting point loses water, yielding dehydrotrimethylbrazilone, $C_{19}H_{16}O_5$. This series of changes can be explained by Feuerstein and Kostanecki's formula on the assumption that during oxidation rearrangement occurs in such a manner that a new central ring is produced.



$$O<\begin{array}{l}C_6H_3(OMe)\\CH_2—CO\end{array}>CH\cdot CH_2\cdot C_6H_3(OMe)_2 \quad \rightarrow$$

I.

$$O<\begin{array}{l}C_6H_3(OMe)\\CH:C(OH)\end{array}>C(OH)\cdot CH_2\cdot C_6H_3(OMe)_2 \quad \rightarrow$$

II.

$$\begin{array}{l}O\cdot CH:C——C_6H_2(OMe)_2\\ |\qquad\quad |\qquad\qquad |\\ OMe\cdot C_6H_3—C(OH)\cdot CH_2\end{array} \quad \rightarrow \quad \begin{array}{l}O\cdot CH:C\cdot C_6H_2(OMe)_2\\ |\qquad\quad |\qquad |\\ OMe\cdot C_6H_3—C:CH\end{array}$$

III. IV.

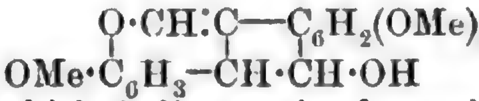
$$\rightarrow \quad \begin{array}{l}O\cdot CH:C——C_6H_2(OMe)_2.\\ |\qquad\quad |\qquad\qquad |\\ OMe\cdot C_6H_3—C(OH)\cdot CH\cdot OH\end{array}$$

V.

The last formula represents trimethylbrazilone, whilst the fourth indicates the product of its dehydration.

Acetyltrimethyldehydrobrazilone (m. p. 176°), already studied by

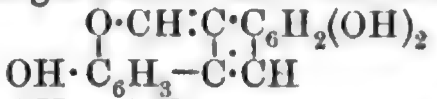
Herzig and by Gilbody and Perkin, when reduced with fuming hydriodic acid, loses its methyl and acetyl groups and becomes converted into a *compound*, $C_{16}H_{10}O_5$, which crystallises in needles containing $1H_2O$ and decomposing indefinitely between 250° and 315°; this substance dissolves in sodium hydroxide to a colourless solution which absorbs oxygen and becomes brownish-red; the alcoholic solution develops a green coloration with ferric chloride. With acetic anhydride and sodium acetate, the reduction product yields a *tetra-acetyl* derivative crystallising from glacial acetic acid in white needles melting at 239—240°.

The following modified formula, 

$$\begin{array}{l}\mathrm{\quad\;\; O\cdot CH{:}C{-\!\!-}C_6H_2(OMe)_2} \\ \mathrm{OMe\cdot C_6H_3{-}CH\cdot CH\cdot OH}\end{array}$$

for trimethylbrazilin is now suggested, which indicates the formation of the new ring. G. T. M.

Brazilin. By E. Bollina, Stanislaus von Kostanecki, and Josef Tambor (*Ber.*, 1902, **35**, 1675—1678. Compare preceding abstract).—The oxidation product of trimethylbrazilin (trimethylbrazilone), when heated with fuming hydriodic acid, loses its methyl radicles and becomes simultaneously dehydrated and reduced; the product formed as a result of these changes should have the formula

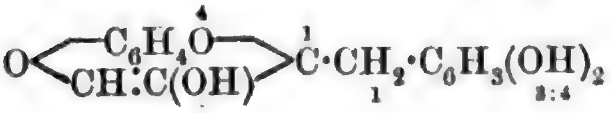


$$\begin{array}{l}\mathrm{\qquad\;\; O\cdot CH{:}C\cdot C_6H_2(OH)_2} \\ \mathrm{OH\cdot C_6H_3{-}C\cdot CH}\end{array}$$

(compare with formulæ IV and V in preceding abstract); the *compound* $C_{16}H_{10}O_4$ is obtained from dilute alcohol in grey leaflets melting at 350°; its solution in sodium hydroxide is colourless with a blue fluorescence and the alcoholic solution develops, with ferric chloride, a blue coloration which changes to green. The *triacetyl* derivative, obtained by the action of sodium acetate and acetic anhydride, crystallises in white needles and melts at 245°.

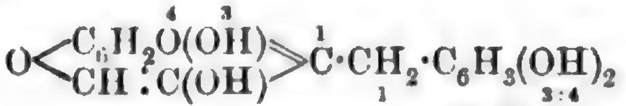
Trimethylbrazilone, on treatment with cold nitric acid of sp. gr. 1·3, changes quantitatively into a *compound*, $C_{19}H_{19}O_9N$, which crystallises from glacial acetic acid and alcohol in yellow needles melting at 225°. The solution of this substance in dilute alkali hydroxide solution has a deep purple colour and when gently warmed yields *p*-methoxysalicylic acid and two neutral *compounds* melting at 122° and 206°, the acidic substance being the principal product.

The communication concludes with a discussion of the constitutions of brazilein and hæmatein, for which the following formulæ



$$\mathrm{O}\left\langle\begin{array}{l}\mathrm{{-}C_6H_4\overset{4}{O}{-}} \\ \mathrm{CH{:}C(OH)}\end{array}\right\rangle\mathrm{\overset{1}{C}\cdot \underset{1}{CH}_2\cdot C_6H_3\underset{3:4}{(OH)_2}}$$

and



$$\mathrm{O}\left\langle\begin{array}{l}\mathrm{C_6H_2\overset{4}{O}\overset{3}{(OH)}} \\ \mathrm{CH\,{:}C(OH)}\end{array}\right\rangle\mathrm{\overset{1}{C}\cdot \underset{1}{CH}_2\cdot C_6H_3\underset{3:4}{(OH)_2}}$$

are respectively suggested. G. T. M.

Brazilin and Hæmatoxylin. Part VII. By Josef Herzig and Jacques Pollak (*Monatsh.*, 1902, **23**, 165—179. Compare Abstr., 1901, i, 478)—Simultaneous reduction and acetylation of brazelein leads to a *triacetyl* derivative, $C_{16}H_9O(OAc)_3$, which crystallises from alcohol, ethyl acetate, or acetic acid in white, glistening leaflets which darken at 170° and melt at 190—195°. Attempts to further acetylate, or to reduce and acetylate, it were without success. When hydrolysed with alkalis, it forms a red solution from which an amorphous substance is precipitated by addition of acid. On hydrolysis with sulphuric acid in acetic acid solution, a crystalline substance separates having the composition of an additive product of brazilein and sulphuric, acid $C_{16}H_{12}O_5,H_2SO_4$. An additive product, $C_{16}H_{12}O_5,HCl$, is formed by treating brazilein with hydrogen chloride in presence of alcohol. With acetic anhydride, sodium acetate, and zinc dust, it yields a product apparently identical with the triacetyl derivative. The oxidation of acetyltrimethylbrazilin yields a substance having the composition of trimethylbrazilin and not of acetyltrimethyldehydrobrazilin (compare Abstr., 1896, i, 379); this product forms colourless crystals which decompose at 150—160° and at 160—170° resolidify to trimethyldehydrobrazilin. As Gilbody and Perkin (Proc., 1899, **15**, 27) find trimethylbrazilone to form straw coloured needles melting at 191°, the authors term their product *β-trimethylbrazilone*. It is also formed by the oxidation of trimethylbrazilin. From the solution of β-trimethylbrazilone in warm alkali, acids precipitate a substance melting at 193—195°, which on acetylation yields acetyltrimethyldehydrobrazilin and is therefore probably trimethyldehydrobrazilin. Acetylation of β-trimethylbrazilone yields acetyltrimethyldehydrobrazilin. Reduction as also reduction and acetylation lead to an amorphous product.

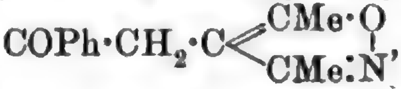
Acetyl-β-trimethyldehydrobrazilin, $C_{16}H_9O(OMe)_3\cdot OAc$, formed by acetylation of the product of the action of concentrated sulphuric acid and alcohol on β-trimethylbrazilone, melts at 183—185°. With potassium hydroxide and methyl iodide, it yields *β-tetramethyldehydrobrazilin*, which melts at 156—159°.

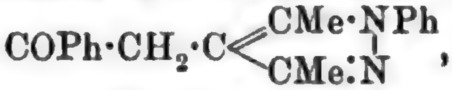
a-Tetramethyldehydrobrazilin is formed by the action of potassium hydroxide and methyl iodide on acetyl-α-trimethyldehydrobrazilin; it melts at 163—165°. The action of potassium hydroxide and methyl iodide on β-trimethylbrazilone yields *α- and γ-tetramethyldehydrobrazilins*, which melt at 130—135°. G. Y.

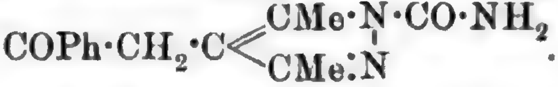
Nitration of Furfuran and a Derivative of Nitrosuccinaldehyde. By R. Marquis (*Compt. rend.*, 1902, **134**, 776—777).—The thick, unstable, non-crystallisable, and non-volatile liquid obtained by the action of nitric acid on furfuran (Abstr., 1901, i, 222) readily reduces Fehling's solution and ammoniacal silver nitrate in the cold and forms a crystalline phenylhydrazone. It seems to be a *nitrosuccinaldehyde monoacetin*, $OH\cdot CH\colon C(NO_2)\cdot CH\colon CAc\cdot OH$ or

$$CHO\cdot CH(NO_2)\cdot CH\colon CAc\cdot OH,$$

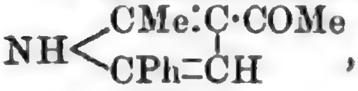
and this view is confirmed by analysis and cryoscopic determinations. When boiled with water, it loses nitrogen oxides and yields an aldehyde which forms a hydrazone containing no oxygen. In the nitration of furfuran in the presence of acetic anhydride, the nucleus is broken and nitrosuccinaldehyde monoacetin is formed, but on treatment with pyridine (*loc. cit.*), the nucleus is again closed with production of nitrofurfuran ($NO_2 = 3$ or 4). C. H. B.

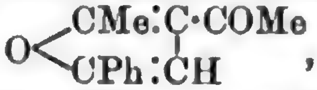
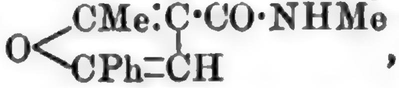
Benzoyldiacetylethane and Acetylmethylfurfuran. By FR. MARCH (*Compt. rend.*, 1902, **134**, 843—845. Compare Abstr., 1901, i, 596).—The triketone, benzoyldiacetylethane, and hydroxylamine yield 4-*phenacyl*-3 : 5-*dimethylisooxazole*,  $COPh\cdot CH_2\cdot C{<}\begin{array}{l}CMe\cdot O\\ CMe:N\end{array}$, which crystallises in slender needles melting at 124—125°; when the triketone is treated with excess of hydroxylamine, the *oxime* of the *iso*oxazole is produced; it crytallises well and melts at 131°.

The compound (m. p. 87—88°) obtained by the action of phenylhydrazine on the triketone is now shown to be 1-*phenyl*-4-*phenacyl*-3 : 5-*dimethylpyrazole*,  $COPh\cdot CH_2\cdot C{<}\begin{array}{l}CMe\cdot NPh\\ CMe:N\end{array}$, whilst the compound (m. p. 262—264°) produced by the action of semicarbazide on the triketone is 4-*phenacyl*-3 : 5-*dimethylpyrazole*-1-*carboxylamide*,

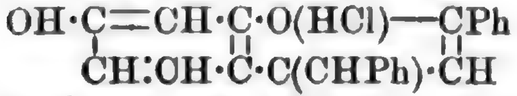


$$COPh\cdot CH_2\cdot C{<}\begin{array}{l}CMe\cdot N\cdot CO\cdot NH_2\\ CMe:N\end{array}.$$

With ammonia, the triketone yields 4-*acetyl*-2-*phenyl*-5-*methylpyrrole*,  $NH{<}\begin{array}{l}CMe:C\cdot COMe\\ CPh{=}CH\end{array}$, which crystallises in slender needles melting at 177—178°.

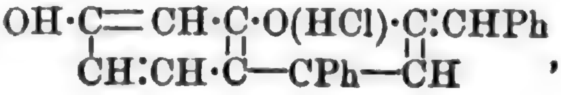
By the action of zinc chloride on a solution of the triketone in acetic acid, or, better, by distilling the triketone under reduced pressure, 4-*acetyl*-2-*phenyl*-5-*methylfurfuran*,  $O{<}\begin{array}{l}CMe:C\cdot COMe\\ CPh:CH\end{array}$, is formed, and crystallises in needles melting at 56—57°, and boils at 179° under 18 mm. pressure; the *semicarbazone* melts at 251—252°, the *oxime* at 111—112°. The last-mentioned substance undergoes the Beckmann transformation under the action of phosphorus pentachloride, yielding an *amide*,  $O{<}\begin{array}{l}CMe:C\cdot CO\cdot NHMe\\ CPh{=}CH\end{array}$, which melts at 146—148°. K. J. P. O.

Condensation Product from Phenylacetylacetophenone and Resorcinol. By CARL BÜLOW and HANS GROTOWSKY (*Ber.*, 1902, **35**, 1519—1528. Compare Abstr., 1901, i, 400, 559, 603, and this vol., i, 112, 113).—7-*Hydroxy*-2-*phenyl*-4-*benzylidene*-1 : 4-*benzopyranol hydrochloride*, produced by passing hydrogen chloride into a glacial acetic acid solution of phenylacetylacetophenone and resorcinol, crystallises from a mixture of alcohol and hydrochloric acid in yellowish-red needles containing $2H_2O$. The substance may be represented by one or other of the formulæ:



$$\begin{array}{l}OH\cdot C{=}CH\cdot C\cdot O(HCl){-}CPh\\ CH:CH\cdot C\cdot C(CHPh)\cdot CH\end{array}$$

or



$$\begin{array}{l}OH\cdot C{=}CH\cdot C\cdot O(HCl)\cdot C:CHPh\\ CH:CH\cdot C{-}CPh{-}CH\end{array},$$

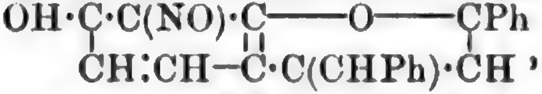
the former being the more probable.

The free *pyranol* could not be obtained crystalline; the *picrate* is insoluble in the ordinary organic solvents and decomposes at 208°.

The *acetyl* derivative of the pyranol, obtained by the action of acetic anhydride and sodium acetate, is soluble in the ordinary organic solvents, crystallises in yellow needles, and melts at 125—127°. The corresponding *benzoyl* derivative, $C_{22}H_{15}O\cdot OBz$, separates from alcohol in greenish-yellow needles and melts at 189°.

7-*Methoxy*-2-*phenyl*-4-*benzylidene*-1 : 4-*benzopyranol*, prepared by the action of sodium methoxide and methyl iodide on the pyranol hydrochloride, crystallises from alcohol in yellow needles melting at 107—108·5°.

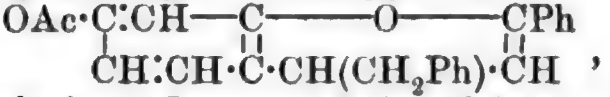
8-*Nitroso*-7-*hydroxy*-2-*phenyl*-4-*benzylidene*-1 : 4-*benzopyranol*,



$$\begin{array}{l} OH\cdot C\cdot C(NO)\cdot C\text{——}O\text{——}CPh \\ CH\!:\!CH{-}C\cdot C(CHPh)\cdot CH \end{array},$$

obtained by treating the pyranol hydrochloride with a cold aqueous solution of sodium nitrite, is a red powder soluble in most organic solvents except light petroleum; it decomposes at 172°. All the preceding compounds except the last exhibit a green fluorescence when dissolved in concentrated sulphuric acid.

7-*Acetoxy*-2-*phenyl*-4-*benzyl*-1 : 4-*benzopyranol*,



$$\begin{array}{l} OAc\cdot C\!:\!CH\text{—}C\text{———}O\text{———}CPh \\ CH\!:\!CH\cdot C\cdot CH(CH_2Ph)\cdot CH \end{array},$$

produced by reducing 7-acetoxy-2-phenyl-4-benzylidene-1 : 4-benzopyranol with zinc dust and a mixture of acetic acid and its anhydride, is a white, amorphous substance which sinters at 60° and melts indefinitely at high temperatures.

The pyranol hydrochloride, when heated with a strong solution of sodium hydroxide, yields a mixture of acetophenone, and ω-phenylresacetophenone, together with traces of resorcinol and benzoic acid. This hydrolysis is evidence in favour of the first formula suggested for the pyranol. G. T. M.

Action of Caro's Reagent on Alkaloids. By E. SPRINGER (*Chem. Centr.*, 1902, i, 761—762; from *Pharm. Zeit.*, 47, 157).—The results of experiments on the behaviour of alkaloids with Caro's reagent (compare Abstr., 1900, i, 133) and also with a mixture of a 5 per cent. aqueous solution of hydrogen peroxide with five times its weight of concentrated sulphuric acid (compare Abstr., 1900, i, 206) show that neither of these reagents furnishes a characteristic test for individual alkaloids, brucine being the only one which gave a very distinct and characteristic coloration. The use of colloidal platinum as recommended by Bredig also failed to produce more intense colorations. Caro's reagent appeared to be a stronger oxidising agent than hydrogen peroxide and sulphuric acid. E. W. W.

Caffeine Iodides. By A. FAUCON (*J. Pharm. Chim.*, 1902, [vi], 15, 370—373).—'Caffeine iodide' (hydriodide of tetraiodocaffeine) is a very unstable compound and always contains a considerable proportion of free iodine. H. R. LE S.

Acyl Derivatives of the Cinchona Alkaloids. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 128116. Compare Abstr., 1901, i, 738, 739).—The acyl derivatives of the cinchona alkaloids may be readily obtained by heating these bases with the aryl esters of the organic acids either alone or in a suitable solvent.

Acetylquinine results from the interaction of quinine and phenyl acetate at 120—130°; the benzoyl derivative is obtained by the agency of phenyl benzoate.

Quinine ethyl carbonate is produced from the alkaloid by heating it with phenyl ethyl carbonate. *Quininecarbamide*, $C_{20}H_{23}ON_2\cdot CO\cdot NH_2$, prepared by the action of phenyl carbamate, separates from dilute alcohol in colourless crystals and melts at 210°.

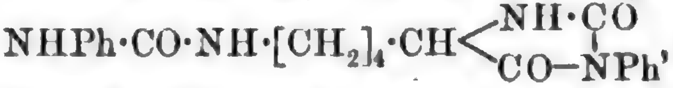
Salicylylquinine, $C_{20}H_{23}ON_2\cdot CO_2\cdot C_6H_4\cdot OH$, prepared by the interaction of the alkaloid and salol, separates from dilute alcohol in colourless crystals melting at 140°. *Salicylylquinidine*, produced in a similar manner, is isolated in the form of its *salicylate*, a salt crystallising from alcohol in white needles melting at 168°.

Cinnamylquinine, $C_{20}H_{23}ON_2\cdot CO_2\cdot CH{:}CHPh$, obtained by the action of phenyl cinnamate, crystallises from ether in slender, white needles and melts at 111°. *Succinylquinine*, $C_2H_4(CO_2\cdot C_{20}H_{23}ON_2)_2$, produced in a similar manner, is readily soluble in most organic solvents and crystallises in needles melting at 97°. G. T. M.

Benzoyllupinine. EMANUEL MERCK (D.R.-P. 129561).—*Benzoyllupinine*, $C_{10}H_{18}ONBz$, obtained either by heating lupinine with benzoyl chloride or benzoic anhydride or by subjecting the base to the Schotten-Baumann reaction, crystallises from dilute alcohol in colourless needles melting at 48—49°, and is extremely soluble in the ordinary organic solvents but does not dissolve in water.

The *hydrochloride* separates in colourless leaflets which are very soluble in water or alcohol; it melts at 208°. G. T. M.

Detection of Lysin and Ornithin. By R. O. HERZOG (*Zeit. physiol. Chem.*, 1902, **34**, 525—527).—Lysin and ornithin readily form additive products with phenylthiocarbamide, but as these do not crystallise at all well, they are not of much value for the detection of the bases. On treatment with concentrated hydrochloric acid, the additive products yield hydantoins, which crystallise remarkably well.

The product from lysin,  $NHPh\cdot CO\cdot NH\cdot[CH_2]_4\cdot CH<\begin{matrix}NH\cdot CO\\ CO—NPh\end{matrix}$, crystallises from a mixture of alcohol and acetone and melts at 183—184°. The corresponding compound from ornithin melts at 191—192°. J. J. S.

Substances contained in Plants. By PAUL SIEDLER (*Chem. Centr.*, 1902, i, 823; from *Ber. Pharm. Ges.*, 12, 64—84).—[With KÖRNER.]—0·04 per cent. of *tanacetine-Riedel*, has been isolated from the flowers of *Tanacetum vulgare*. This alkaloid or mixture of alkaloids forms a viscous, oily liquid, has a bitter, burning taste, is very slightly soluble in water, but readily so in alcohol or ether, is very volatile in steam, and combines with inorganic acids to form very hygroscopic salts.

The roots of *Cynoglossum officinale* yield 0·12 per cent. of an alkaloid *cynoglossine-Riedel*, which, when freshly prepared, forms a clear, viscous liquid, has an extremely bitter taste, and a distinct narcotic odour similar to that of pelletierine, is rather soluble in water, soluble in all proportions of ether, alcohol, or chloroform, and forms well characterised salts with mineral acids. According to Kobert, tanacetine and cynoglossine have only very weak physiological action.

[With WINZHEIMER.]—Agaricic acid (compare Jahns, Abstr., 1884, 353; Schmieder, *Arch. Pharm.*, 1886, **224**, 641) crystallises with $1\frac{1}{2}H_2O$, is only very slightly decomposed at 100°, and forms clear solutions in alkali carbonates. The normal salts are readily soluble in water, forming faintly alkaline solutions which only become clear, however, on the addition of a small excess of alkali. Attempts to decompose the normal salt with elimination of water by heating above 120°, according to Jahns' and Schmieder's method, failed. Sodium hydrogen agaricate softens at 160° and decomposes and melts about 180°, whilst the potassium salt melts at 200° without previously softening. The carboxyl groups of the acid do not appear to have equal values. The *normal* and *basic bismuth* salts, $Bi_2C_{48}H_{84}O_{15}$, $BiC_{16}H_{29}O_6$, and $BiC_{16}H_{29}O_6 \cdot BiO \cdot OH$, resist the action of dilute acids to an extraordinary extent, and have an astringent action. *Bismuth diagaricate monotannate*, $BiC_{30}H_{37}O_{14}$, *basic bismuth agaricate tannate*, $Bi_2C_{44}H_{46}O_{24}$, and *bismuth monoagaricate ditannate*, $Bi_2C_{72}H_{64}O_{41}$, have similar physiological effects. *Bismuth hydroxy-iodide agaricate*,

$$OH \cdot C_{14}H_{27}(CO_2H) \cdot CO \cdot O \cdot Bi(OH)I,$$

is a pale grey powder corresponding with airol. Diethyl agaricate and dimethyl agaricate melt at 36—37° and 62—62·5° respectively. Acetylagaric acid melts at 81°. When agaricic acid is heated at 140—160°, a sand coloured compound melting at 30° is formed; the composition of this substance does not agree with that of an anhydride. *Agaricic diphenetidide*, $OH \cdot C_{14}H_{27}(CO \cdot C_8H_{10}ON)_2$, and *agaricic monophenetidide*, $OH \cdot C_{14}H_{27}(CO_2H) \cdot CO \cdot C_8H_{10}ON$, are prepared by condensing the acid with *p*-phenetidine at 140—160°. The former is a bluish-white, crystalline powder, melts at 151°, and is only slightly soluble in organic solvents, whilst the latter is an almost colourless, crystalline powder, contains water, and is readily soluble in organic solvents; the anhydrous salt melts at 100°. Different products are obtained when the condensation with *p*-phenetidine is effected at 200°.

Körner has found that the proportions of emetine, cephæline and psychotrine (compare Paul and Cownley, *Amer. J. Pharm.*, **73**, Nos. 1, 2, 3) contained in Rio ipecacuanha bark are as 1 : 0·5 : 0·1 respectively, and in Carthagena bark 1 : 1 : 0·2. E. W. W.

Methylenedipiperidine. By ERNST SCHMIDT (*Arch. Pharm.*, 1902, **240**, 230—231).—An introduction to the paper with which the following abstract deals. C. F. B.

Methylenepiperidines of Various Origin. By PAUL KÖHLER (*Arch. Pharm.*, 1902, **240**, 231—240).—Methylenedipiperidine, $CH_2(C_5NH_{10})_2$, was prepared by warming piperidine with trioxymethylene (Ehrenberg, Abstr., 1887, 1026); by treating piperidine with methylene iodide, or boiling it with methylene chloride, in alcoholic solution (Trebst, *Inaug. Diss. Jena*, 1890); and by mixing piperidine with aqueous sodium hydroxymethylsulphonate (formaldehyde sodium hydrogen sulphite; Kraut, Abstr., 1890, 1092). An identical product is obtained in all cases, boiling at 230—231° and having a sp. gr. 0·920—0·921 at 15°.

Methylenedipiperidine is a diacid base, but its salts are very unstable, decomposing with formation of piperidine salts. By neutralising it in alcoholic solution with hydrogen chloride and allowing the solution to evaporate in a desiccator, a mixture of its chloride with that of piperidine was apparently obtained; the *aurichloride* forms a flocculent precipitate and melts at 210—214°. A platinichloride could not be obtained. When treated with methyl iodide in alcoholic solution, methylenedipiperidine forms the *monohydriodide*, which melts at 125°, and methylpiperidine methiodide, $C_5NH_{10}Me,MeI$ (the *aurichloride* corresponding with which melts at 278°), together with piperidine hydriodide. C. F. B.

Preparation of *n*-Methylgranatanine by the Electrolytic Reduction of *n*-Methylgranatonine. By ANTONIO PICCININI (*Gazzetta*, 1902, **32**, i, 260—265).—When electrolysed in dilute sulphuric acid solution, *n*-methylgranatonine is converted almost quantitatively into *n*-methylgranatanine, no intermediate products being apparently formed. The reduction may also be effected by means of zinc dust and dilute sulphuric acid. T. H. P.

[Electrolytic Reduction of Pyrroles.] MAXIMILIANO DENNSTEDT (D.R.-P. 127086).—The reduction of pyrrole and its homologues to the corresponding dihydro-derivatives is readily effected by suspending the substance in dilute sulphuric acid contained in the cathode cell of an electrolytic apparatus, the cathode being of lead and the current having a density of 1 ampere per sq. cm.

In this manner, pyrrole readily yields dihydropyrrole, and ethylpyrrole gives rise to dihydroethylpyrrole, the platinichloride, $(C_6H_{11}N)_2,H_2PtCl_6$, of which forms yellow needles melting at 170°. Diethylpyrrole may be similarly reduced. G. T. M.

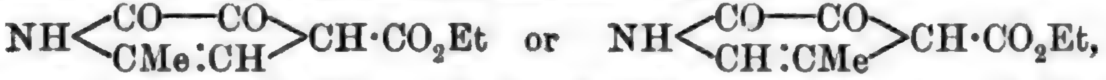
Studies in the Furfuran and Pyrrole Groups. I. By FRANZ FEIST (*Ber.*, 1902, **35**, 1537—1544).—A discussion of the various syntheses of furfuran- and pyrrole-carboxylic acids and of the author's own results, which are detailed in the following three abstracts.

R. H. P.

Studies in the Furfuran and Pyrrole Groups. II. Condensation of Esters of β-Ketonic Acids with Chloroacetone and Ammonia. By FRANZ FEIST [and, in part, B. WIDMER and R. DUBUSC] (*Ber.*, 1902, **35**, 1545—1556).—The condensation of ethyl acetoacetate with chloroacetone and ammonia yields, in addition to ethyl 2 : 5-dimethylpyrrole-3-carboxylate (Hantzsch, Abstr., 1890, 1155), *ethyl 2 : 4-dimethylfurfuran-3-carboxylate*, which is an oil boiling at 97° under 10 mm. pressure, and is always obtained contaminated with another *compound*, $C_7H_{14}O_4$ (?); the latter is either a diketone or ketone-alcohol and crystallises in lustrous leaflets melting at 80°. The analogous condensation with aniline yields *ethyl* 1-*phenyl*-2 : 5-*dimethylpyrrole*-3-*carboxylate*; this distils at 225° under 40 mm. pressure, and when cold solidifies to white crystals melting at 43°; it is soluble in organic solvents, and when hydrolysed yields the corresponding *acid*, which crystallises from alcohol and melts and decomposes at 205°.

The *barium, silver, silver hydrogen*, and *silver ethyl* salts of 3-carboxy-2-methylfurfuran-4-acetic acid (Abstr., 1899, i, 675) are described; this acid, when boiled with water, yields 2 : 4-dimethylfurfuran-3-carboxylic acid, which forms crystalline *barium* (with $6H_2O$), *calcium* (with $4H_2O$), and *silver* salts, and oily *methyl* and *ethyl* esters.

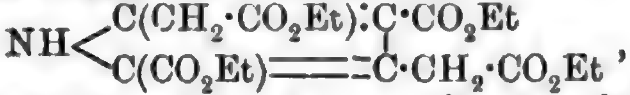
When ammonia is passed into an ethereal solution of ethyl oxalacetate and chloroacetone, condensation ensues with the formation of oxamide and *ethyl oxymethylpyridonecarboxylate*,



$$NH{<}\begin{matrix}CO\text{——}CO\\CMe{:}CH\end{matrix}{>}CH\cdot CO_2Et \quad\text{or}\quad NH{<}\begin{matrix}CO\text{——}CO\\CH{:}CMe\end{matrix}{>}CH\cdot CO_2Et,$$

which dissolves in alkalis, is insoluble in alcohol, melts at 223°, and can be sublimed. The corresponding *acid* crystallises in lustrous, white leaflets (with $2H_2O$), melts and decomposes, when anhydrous, at 255°, and forms *potassium* (decomposing at 283°), *barium*, and *silver* salts. The *amide* is a white powder, soluble in ammonia, and decomposes above 280°. The acid, when heated above its melting point, evolves carbon dioxide and forms *oxymethylpyridone*, $C_6H_7O_2N$, which sublimes in small needles, melts at 201—202°, is soluble in sodium carbonate, and reduces alkaline permanganate and ammoniacal silver oxide solutions. All these pyridone compounds give a green (or greenish-blue) coloration with ferric chloride. R. H. P.

Studies in the Pyrrole Group. III. Condensation of Esters of *iso*Nitroso-β-ketonic Acids with Esters of β-Ketonic Acids by Reduction. By FRANZ FEIST (*Ber.*, 1902, **35**, 1556—1557).—*Ethyl* 3 : 5-*dicarboxypyrrole*-2 : 4-*diacetate*,



$$NH{<}\begin{matrix}C(CH_2\cdot CO_2Et){:}C\cdot CO_2Et\\ C(CO_2Et)\text{====}C\cdot CH_2\cdot CO_2Et\end{matrix},$$

obtained when a mixture of ethyl acetonedicarboxylate and its nitroso-derivative is reduced with zinc dust, melts at 113—113·5°, is soluble in most organic solvents except light petroleum, and is not easily reduced or brominated.

The corresponding *acid* crystallises with H_2O in small needles, which turn red in air and melt and decompose at 220°, yielding 2 : 4-dimethylpyrrole. R. H. P.

Studies in the Pyrrole Group. IV. Condensation of Esters of Amino-β-ketonic Acids with 1 : 2-Diketones and 1 : 2-Ketone-alcohols. By FRANZ FEIST and ERICH STENGER (*Ber.*, 1902, **35**, 1558—1561).—Ethyl aminocrotonate condenses with benzoin, forming *ethyl* 4 : 5-*diphenyl*-2-*methylpyrrole*-3-*carboxylate*, which separates from methyl alcohol in white crystals and melts at 202°. The *acid*, which was only obtained in an impure state, melts at 132° and forms insoluble *silver, calcium*, and *barium* salts.

Analogous condensation with ethyl diketosuccinate yields a mixture of a *compound*, $C_{20}H_{30}O_9N_2$, and *ethyl 2-methylpyrrole-3:4:5-tricarboxylate*; the former crystallises in small, colourless needles melting at 149·5°, and the latter separates from ether in small, lustrous crystals melting at 104°.

Similar condensations with diacetyl, benzil, and phenanthraquinone gave no definite pyrrole derivatives. R. H. P.

Condensation of Pyrroles and Ethereal Pyrrolecarboxylates with Aromatic Aldehydes. By Franz Feist (*Ber.*, 1902, **35**, 1647—1655. Compare preceding abstract).—The condensation between pyrrole derivatives and the aldehydes obeys the following rules: (1) only those derivatives condense which contain at least one hydrogen atom combined with a carbon atom of the nucleus; this atom may be either in the α- or the β-position; (2) when both α- and β-positions are occupied by substituents, no combination occurs even when an imino-hydrogen atom is present; (3) pyrrole derivatives containing more than one hydrogen atom in the ring may combine with aldehydes in molecular proportions.

These empirical laws indicate that the aldehyde residue at once combines with the carbon atom of the nucleus without forming an intermediate N-derivative. The reaction seems to depend on the reactivity of the double linkings of the pyrrole ring.

The condensations were produced by melting together the pyrrole derivative and the aldehyde and adding some powdered potassium hydrogen sulphate.

[With B. Widmer and J. Sakowitsch.]—*Ethyl phenylmethanebis-2:5-dimethylpyrrole-3-carboxylate*, $CHPh(C_4NHMe_2 \cdot CO_2Et)_2$, prepared from benzaldehyde and 2:6-dimethylpyrrolecarboxylate, crystallises from dilute alcohol in lustrous leaflets melting at 228°; it is insoluble in water and not hydrolysed by mineral acids.

Ethyl p-*nitrophenylmethanebis-2:5-dimethylpyrrole-3-carboxylate*, $NO_2 \cdot C_6H_4 \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$, crystallises from alcohol in yellowish-green needles and melts at 275·5°; the *isomeride* from *m*-nitrobenzaldehyde melts at 214°.

Diethyl p-*hydroxy*-m-*methoxyphenylmethanebis-2:5-dimethylpyrrole-3-carboxylate*, $OMe \cdot C_6H_4(OH) \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$, is a crystalline powder obtained by condensation with vanilaldehyde; it melts at 216°.

Ethyl styrylmethanebis-2:5-dimethylpyrrole-3-carboxylate,

$$CHPh{:}CH \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2,$$

from the pyrrole ester and cinnamaldehyde, forms white crystals melting at 243°.

Ethyl o-*hydroxyphenylmethanebis-2:5-dimethylpyrrole-3-carboxylate*, $OH \cdot C_6H_4 \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$, obtained from salicylaldehyde, is a white powder melting at 212°; it develops a deep red coloration either with ferric chloride or atmospheric oxygen.

Ethyl methylenedioxyphenylmethanebis-2:5-dimethylpyrrole-3-carboxylate, $CH_2{:}O_2{:}C_6H_3 \cdot CH(C_4NHMe_2 \cdot CO_2Et)_2$, melts at 110°.

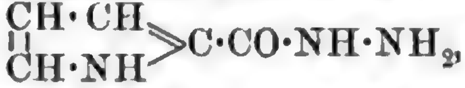
Ethyl phenylmethanebis-2:4-dimethylpyrrole-3-carboxylate, prepared from ethyl 2:4-dimethylpyrrole-3-carboxylate and benzaldehyde, melts at 188°; the *nitro*-compound from *p*-nitrobenzaldehyde crystallises in yellow needles and melts at 192°; anisaldehyde gives a *product* crystallising in white needles and melting at 171—172°.

Ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate and benzaldehyde yield a crystalline condensation *product* melting at 160°; its p-*nitro*-derivative separates in pale yellow needles.

1-*Phenylbenzylidenepyrrole*, formed by the condensation of 1-phenylpyrrole and benzaldehyde, readily dissolves in acetone and separates from a mixture of this solvent with alcohol as a white powder melting at 265·5°; it has not been ascertained whether this compound has the simple formula $CHPh{:}C_4NH_2Ph$, or whether it results from a condensation of 2 mols. of the aldehyde with 2 mols. of the base. Another product is formed in the condensation and is separated from the preceding substance by extraction with petroleum; it separates from this solvent as a pale pink powder melting at 231° and giving analytical figures corresponding with those required for the formula $(C_{18}H_{15}N)_x$.

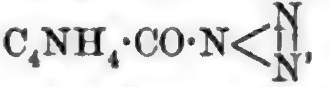
G. T. M.

Hydrazides of 2-Pyrrolecarboxylic Acid and of 2-Indolecarboxylic Acid and their Transformations. By ANTONIO PICCININI and L. SALMONI (*Gazzetta*, 1902, **32**, i, 246—253).—The authors have been unable to prepare the 2-amino-derivatives of pyrrole and indole from the 2-carboxylic acids of these bases, but they have obtained the corresponding hydrazides, azoimides, and urethanes.



Pyrroylhydrazide, $\left.\begin{array}{l}CH\cdot CH\\ \|\\ CH\cdot NH\end{array}\right>C\cdot CO\cdot NH\cdot NH_2$, prepared by the interaction of hydrazine and methyl pyrrole-2-carboxylate, crystallises from dilute alcohol in compact, colourless prisms which become faintly yellow at 210° and melt at 231—232°; it is slightly soluble in methyl or ethyl alcohol or light petroleum and to a greater extent in water. Its aqueous solution energetically reduces Fehling's solution and ammoniacal silver nitrate.

Benzaldehydepyrroylhydrazone, $C_4H_4N\cdot CO\cdot NH\cdot N{:}CHPh$, prepared from pyrroylhydrazide and benzaldehyde, separates from dilute alcohol in shining leaflets melting at 164—165°.



Pyrroylazoimide, $C_4NH_4\cdot CO\cdot N<\begin{array}{l}N\\ \|\\ N\end{array}$, obtained by the action of nitrous acid on pyrroylhydrazide, is deposited in nacreous crystals which melt and evolve gas at 105° and are soluble in alcohol or ether. On reduction with zinc and acetic acid, it is converted into carbopyrrolamide.

1-*Pyrrylurethane*, $C_4NH_4\cdot NH\cdot CO_2Et$, prepared by boiling pyrroylhydrazide with absolute alcohol, nitrogen being at the same time evolved, crystallises from light petroleum in long, colourless needles melting at 55—56° and rapidly changing in the air to a red mass. The action of nitrous acid on its hydrochloric acid solution yields a *nitroso*-derivative which separates from water or alcohol as a microcrystalline powder decomposing without melting at 200—210°. When heated with acetic anhydride, pyrroylurethane yields a crystalline *acetyl* derivative. No definite products are formed when the base is boiled with ammonia, alkalis, or hydrochloric acid.

Indole-1-*carboxylic acid hydrazide*, $C_9H_9ON_3$, separates from alcohol in shining, nacreous leaflets which soften at 230° and melt at 241°; it is slightly soluble in water or hydrochloric or acetic acid and its aqueous solution readily reduces silver nitrate.

Indole-1-*carboxylic acid azoimide*, $C_9H_6ON_4$, separates in colourless leaflets which are slightly soluble in water and decompose violently at about 140°.

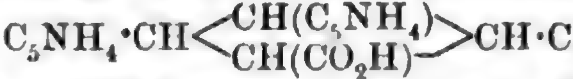
1-*Indole-urethane*, $C_{11}H_{12}O_2N_2$, crystallises from light petroleum in compact, colourless prisms melting at 110°, and shows reactions similar to those of the pyrrole compound. T. H. P.

Some Compounds of Pyridine. By J. Arthur Hayes (*J. Amer. Chem. Soc.*, 1902, **24**, 360—362).—When a solution of antimony tribromide in hydrobromic acid is added to a solution of pyridine hydrobromide, the *compound*, $C_5NH_5,SbBr_3,3HBr$, is obtained as a yellow, crystalline precipitate, which is soluble in dilute hydrochloric acid and slightly so in alcohol or chloroform.

The *compound*, $C_5NH_5,SnCl_2,3HCl$, obtained in a similar manner, crystallises in small, white needles, and is soluble in dilute hydrochloric acid, and slightly so in alcohol.

The *compound*, $C_5NH_5,MnCl_2,HCl$, crystallises in salmon-coloured plates and is soluble in alcohol or hydrochloric acid, and slightly so in ether. E. G.

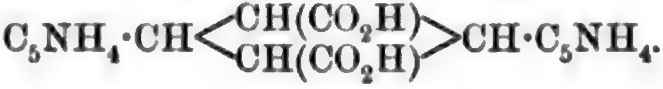
Some Derivatives of α-Picoline. By Karl Feist (*Arch. Pharm.*, 1902, **240**, 178—201. Compare Hardy and Calmels, Abstr., 1887, 1057, and Knudsen, Abstr., 1895, i, 564).—γ-Trichloro-α-hydroxypropylpyridine (Einhorn, Abstr., 1892, 75) was prepared, and its *aurichloride*, melting at 152°, *platinichloride*, with $1\frac{1}{2}H_2O$, *picrate*, melting at 167°, and the compound, $C_8H_8ONCl_3,5HgCl_2$, melting at 148° were analysed. The hydrochloride of pyridylacrylic acid is converted into the acid itself, when it is recrystallised from absolute alcohol. The acid is merely converted into the *hydriodide*, which melts at 196—197°, by aqueous hydriodic acid at the ordinary temperature; when it is boiled with hydriodic acid in acetic acid solution, it is reduced to 2-*pyridyl-β-propionic acid*. This melts at 141°; its *aurichloride*, melting at 164°, and *platinichloride*, with $2H_2O$, melting at 177°, were analysed. 2-Pyridyl-β-bromopropionic acid forms an *auribromide*, melting at 151—160°, and readily loses hydrogen bromide with regeneration of pyridylacrylic acid; silver acetate precipitates the bromine and forms pyridyl-β-lactic acid, which is also formed by the action of silver chloride. The bromo-acid reacts with 33 per cent. alcoholic trimethylamine, best at 0—8°, forming, in addition to pyridylacrylic acid, *β-pyridyltruxillic acid*,



$C_5NH_4{\cdot}CH{<}\begin{matrix}CH(C_5NH_4)\\CH(CO_2H)\end{matrix}{>}CH{\cdot}CO_2H$;

the *hydrochloride* of this melts at 209°, the *aurichloride*, with $HAuCl_4$, at 182°, and the *platinichloride*, with H_2PtCl_6, at 185—186°. The proportion converted into pyridylacrylic acid is increased when the trimethylamine is allowed to react at a higher temperature, or in aqueous instead of alcoholic solution.

2-Pyridyl-α-lactic acid (Einhorn, *loc. cit.*) can be converted into

2-*pyridyl-a-bromopropionic acid* by heating it with phosphorus tribromide at 130—140° in an atmosphere of carbon dioxide in a sealed tube; the *auribromide* of this acid melts at 195°. By alcoholic trimethylamine, the acid is converted almost entirely into an *acid*, which, from the analysis and melting point, 182°, of its *aurichloride*, seems to be identical with β-truxillic acid, but may possibly be *a-truxillic acid*,  $C_5NH_4\cdot CH\left\langle\begin{matrix}CH(CO_2H)\\CH(CO_2H)\end{matrix}\right\rangle CH\cdot C_5NH_4$. C. F. B.

Transformation of Meconic Acid Derivatives into Hydroxypyridines. By ALBERTO PERATONER (*Atti Real. Accad. Lincei*, 1902, [v], 11, i, 327—333).—A *résumé* of the subject. T. H. P.

[Indole Derivatives.] FARBENFABRIKEN VORM. F. BAYER & Co (D.R.-P. 127245 and 128660).—5-*Chloro-2-methylindole*,

$$C_6H_3Cl\left\langle\begin{matrix}NH\\CH\end{matrix}\right\rangle CMe,$$

(compare E. Fischer, Abstr., 1886, 805), prepared by heating the *p*-chlorophenylhydrazone of acetone with zinc chloride, and separated by distillation in steam, crystallises in plates and melts at 119°.

2-*Phenyl*-5-*methylindole*, C_8H_5NMePh, and 5-*chloro*-2-*phenylindole*, C_8H_5NPhCl, are pale yellow, crystalline powders melting at 213° and 96°.

1 : 2 : 5-*Trimethylindole*, $C_8H_4NMe_3$ (E. Fischer, *loc. cit.*), produced from *as-p*-tolylmethylhydrazine and acetone, is readily distilled in steam; it crystallises in colourless leaflets and melts at 56—57°.

2-*Phenyl*-1 : 5-*dimethylindole*, $C_8H_4NMe_2Ph$, obtained from *as-p*-tolyl methylhydrazine and acetophenone, crystallises from dilute alcohol in colourless leaflets and melts at 124°.

5-*Chloro*-1 : 2-*dimethylindole*, $C_8H_4NMe_2Cl$, produced from *as-p*-chlorophenylmethylhydrazine and acetone, forms leaflets melting at 67°.

5-*Chloro*-2-*phenyl*-1-*methylindole*, $C_8H_4NMePhCl$, separates from alcohol in yellow crystals melting at 109°.

2-*Phenyl*-1-*ethylindole* forms colourless crystals melting at 86°.

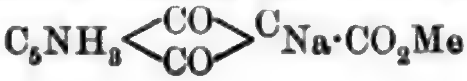
2 : 5-*Dimethyl*-1-*ethylindole*, $C_8H_4NMe_2Et$, and 2-*phenyl*-5-*methyl*-1-*ethylindole*, $C_8H_4NMeEtPh$, form colourless crystals melting respectively at 47° and 72°.

5-*Chloro*-2-*methyl*-1-*ethylindole*, $C_8H_4NMeEtCl$, prepared from *p*-chloro-*as*-ethylphenylhydrazine and acetone, crystallises from light petroleum in rhombic plates and melts at 74°. 5-*Chloro*-2-*phenyl*-1-*ethylindole*, $C_8H_4NEtPhCl$, is an amorphous, yellow powder melting at 107°.

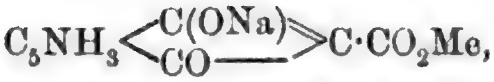
The preceding indole derivatives all give the colour reaction with the pine-wood shaving, and combine with auramine or diaminobenzophenone or its derivatives, yielding basic colouring matters.

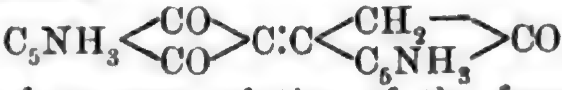
G. T. M.

Synthesis of Pyrindene Derivatives. By KARL BITTNER (*Ber.*, 1902, 35, 1411—1413).—By condensing dimethyl quinolinate with methyl acetate by means of sodium, the *sodium* salt,

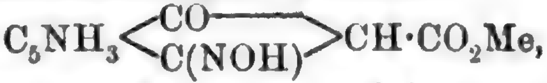


$$C_5NH_3\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CNa\cdot CO_2Me$$

or  $C_5NH_3{<}\begin{matrix}C(ONa)\\ CO\end{matrix}{>}C\cdot CO_2Me$, of *methyl pyrindanedionecarboxylate*, is obtained in the form of yellow needles which rapidly resinify in the air; on acidifying a solution of the *sodium* derivative, yellow crystals of the parent substance, $C_{10}H_7O_4N$, separate; the *barium* salt, $(C_{10}H_6O_7N)_2Ba$, forms yellow needles.

Anhydrobispyrindanedione,  $C_5NH_3{<}\begin{matrix}CO\\ CO\end{matrix}{>}C{:}C{<}\begin{matrix}CH_2\\ C_5NH_3\end{matrix}{>}CO$, obtained by heating a concentrated aqueous solution of the foregoing sodium derivative with glacial acetic acid for several hours at 100°, is insoluble in the ordinary solvents.

Methyl pyrindanedionecarboxylate monoxime,



$$C_5NH_3{<}\begin{matrix}CO\\ C(NOH)\end{matrix}{>}CH\cdot CO_2Me,$$

obtained from the sodium derivative and hydroxylamine, crystallises from water in yellow needles; a dioxime could not be obtained.

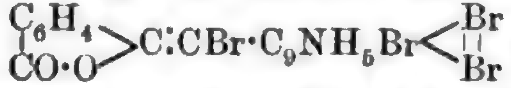
W. A. D.

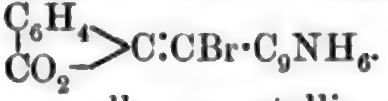
Nitroquinolones and Nitrocarbostyrils. By Herman Decker (*J. pr. Chem.*, 1902, [ii], **65**, 300—303. See Abstr., 1902, i, 654).—*Trinitro*-1-*methyl*-2-*quinolone*, obtained when 5-nitro-1-methyl-2-quinolone is treated with fuming nitric acid, separates from toluene either in lustrous, pointed needles with toluene of crystallisation, or in short, yellow, compact prisms; it melts and decomposes at 221°. The analogous *trinitro*-1-*ethyl*-2-*quinolone* crystallises with toluene and melts and decomposes at 222°.

6-Nitro-1-ethyl-2-quinolone, when treated with nitric acid in the cold, forms a *nitrate* which crystallises in bright yellow needles and melts at 183°.

Dinitro-1-*ethyl*-2-*quinolone*, obtained along with the trinitro-compound when 5-nitro-1-ethyl-2-quinolone is nitrated with warm fuming nitric acid, crystallises from alcohol in large, pointed needles, turns brown at 175—180°, sinters at 192°, and melts and decomposes at 197°.

R. H. P.

Bromo-derivatives of Quinophthalone. By Alexander Eibner and H. Merkel (*Ber.*, 1902, **35**, 1656—1662. Compare Abstr., 1901, i, 611).—The compound obtained by mixing a chloroform or glacial acetic acid solution of quinophthalone and bromine is not a tribromoquinophthalone, but contains four atoms of bromine; it is, however, very unstable, losing bromine at the ordinary temperature and parting with the whole of the halogen on gentle warming; all the solvents affect it except chloroform, from which it separates in orange-yellow crystals. The following reactions indicate that it is a perbromide, and that the formula  $\begin{matrix}C_6H_4\\ CO\cdot O\end{matrix}{>}C{:}CBr\cdot C_9NH_5Br{<}\begin{matrix}Br\\ Br\end{matrix}$ best expresses its behaviour. The substance, when treated with water or alcohol, yields bromoquinophthalone; ammonia or sulphurous acid, on warming, removes the halogen regenerating quinophthalone; iodine is liberated from an acid solution of potassium iodide. Treatment with cold ammonia indicates that two bromine atoms are in the "perbromide" condition, for 2 mols. of this reagent are decomposed with the evolution of nitrogen by 3 mols. of the bromo-derivative.

Bromoquinophthalone is most readily obtained by the action of alcohol or ammonia on the tetrabromide at the ordinary temperature, and crystallises from chloroform in pale yellow, hexagonal plates melting at 179°; its hydrobromide is an unstable, red salt which is formed, together with the preceding perbromide, by the action of bromine on quinophthalone, and decomposes at 100° into quinophthalone and bromine. The *perbromide* of bromoquinophthalone, $C_{18}H_{11}O_2NBr_6$, results from the action of bromine in chloroform solution; it is very unstable, losing bromine at the ordinary temperature, and is decomposed by alcohol, water, or ammonia. These reactions indicate that the preceding bromoquinophthalone has the formula  $\begin{matrix}C_6H_4\\CO_2\end{matrix}\!\!>C\colon CBr\cdot C_9NH_6$.

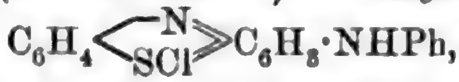
p-Toluquinophthalone also yields an orange-yellow, crystalline *tetrabromide*, $C_{19}H_{13}O_2NBr_4$. G. T. M.

Dinitrocarbazole. ERNST WIRTH (D.R.-P. 128853).—A *dinitrocarbazole* is readily prepared by agitating a 10 per cent. benzene solution of nitrosocarbazole (obtained by treating crude carbazole with nitrous acid) with nitric acid of sp. gr. 1·36 until a green coloration is no longer developed with concentrated sulphuric acid. The product is sparingly soluble in the ordinary solvents, but dissolves in hot nitrobenzene or aniline, and separates on cooling as a yellow powder not melting below 320°. On reduction, it yields diaminocarbazole.

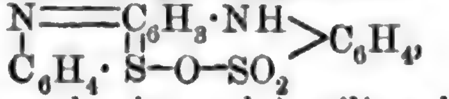
G. T. M.

9-Iodoacridine. KALLE & Co. (D.R.-P. 126795. Compare Abstr., 1901, i, 166).—9-*Iodoacridine*, prepared by heating together alcoholic solutions of 9-bromoacridine and sodium iodide, separates in a crystalline form and melts at 171°; the yield is practically quantitative.

G. T. M.

Thiazine Colouring Matters. AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 126410).—*Phenylthiazine* (3-*anilinophenazothionium chloride*),  $C_6H_4\!<\!\begin{matrix}N\\SCl\end{matrix}\!>\!C_6H_3\cdot NHPh$, readily obtained from thiodiphenylamine, aniline (1 mol.), and alcoholic ferric chloride, crystallises from dilute hydrochloric acid in coppery leaflets which dissolve in water or alcohol to a bluish-green solution; the free thio-base is precipitated by ammonia or the alkali hydroxides in pink flocks.

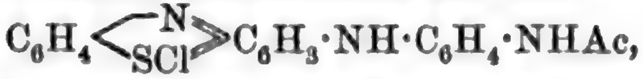
3-*Anilinophenazothionium anhydrosulphonate*,



$$\begin{matrix}N & = & C_6H_3\cdot NH\\ | & & \|\\ C_6H_4\cdot & & S-O-SO_2\end{matrix}\!>\!C_6H_4,$$

produced from thiodiphenylamine, sulphanilic acid, and ferric chloride, is a dark green, crystalline powder.

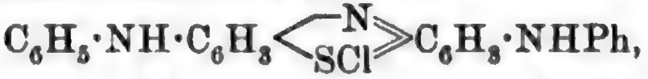
3-p-*Acetylanilinoaminophenazothionium chloride*,



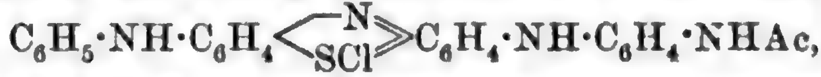
$$C_6H_4\!<\!\begin{matrix}N\\SCl\end{matrix}\!>\!C_6H_3\cdot NH\cdot C_6H_4\cdot NHAc,$$

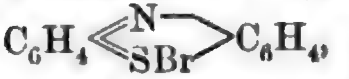
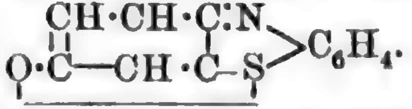
obtained in a similar manner from monoacetyl-*p*-phenylenediamine, separates in coppery needles. The preceding compounds dye tannin-mordanted cotton a dark green.

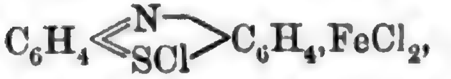
3 : 9-*Dianilinophenazothionium chloride*,



$$C_6H_5\cdot NH\cdot C_6H_3{<}^{N}_{SCl}{>}C_6H_3\cdot NHPh,$$

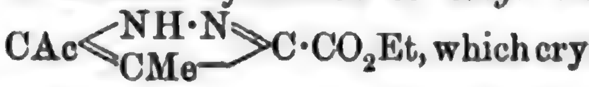
prepared by the action of ferric chloride on 1 mol. of thiodiphenylamine and 2 mols. of aniline, crystallises from hot alcohol in needles having a brass-like lustre which are sparingly soluble in cold water, but dissolve more readily in the boiling solvent or in alcohol. The *monoacetyl* derivative,  $C_6H_5\cdot NH\cdot C_6H_4{<}^{N}_{SCl}{>}C_6H_4\cdot NH\cdot C_6H_4\cdot NHAc$, obtained by heating an alcoholic solution of 4-*p*-acetylanilinoaminophenazothionium chloride with aniline hydrochloride, is precipitated from its blue aqueous solution on adding sodium chloride ; it dissolves in alcohol to a bluish-green solution. G. T. M.

Phenazothionium Salts. Aktiengesellschaft für Anilin-Fabrikation (D.R.-P. 126602).—*Phenazothionium bromide*,  $C_6H_4{<}^{N}_{SBr}{>}C_6H_4$, prepared by mixing together at −15° to −20° alcoholic solutions of thiodiphenylamine and bromine in the presence of a small amount of hydrobromic acid, separates as a brownish-green, crystalline powder with a metallic lustre. The oxidation may also be effected in benzene, chloroform, carbon disulphide, or ethereal solution, and under these conditions the bromide is completely precipitated, being insoluble in these solvents; it undergoes decomposition when dissolved in water or alcohol, but is rendered more stable by the presence of acid. The solution, when boiled, yields a mixture of thiodiphenylamine, and the substance  $\begin{matrix}CH\cdot CH\cdot C{:}N\\ O\cdot C—CH\cdot C–S\end{matrix}{>}C_6H_4$.

The *double salt* of phenazothionium chloride and ferrous chloride,  $C_6H_4{<}^{N}_{SCl}{>}C_6H_4,FeCl_2$, produced by oxidising thiodiphenylamine with an alcoholic solution of ferric chloride acidified with hydrochloric acid, separates as a dark greenish-brown powder.

Phenazothionium picrate, formed when the preceding experiments are carried out in the presence of picric acid, separates out as a yellowish-green powder.

These phenazothionium derivatives yield thiazine colouring matters on condensation with amines. G. T. M.

Pyrazoles from 1 : 3-Diketones and Alkyl Diazoacetates. By August Klages (*J. pr. Chem.*, 1902, [ii], **65**, 387—393. Compare this vol., i, 236).—Acetylacetone and ethyl diazoacetate condense in a warm, very dilute solution of sodium hydroxide to *ethyl 5-acetyl-4-methylpyrazole-3-carboxylate*,  $CAc{<}^{NH\cdot N}_{CMe}{>}C\cdot CO_2Et$, which crystallises from water in long, colourless needles, melts at 123—124°, boils at 202° under 26 mm. pressure, and is easily soluble in alcohol, chloroform, glacial acetic acid, or ammonia. With concentrated aqueous sodium hydroxide, it forms a *sodium* derivative, and with silver nitrate a white, flocculent precipitate, $C_9H_{11}O_3N_2Ag$. A mol. weight determination gave 194; $C_9H_{12}O_3N_2$ requires 196. The *oxime* forms glistening, colourless leaflets which melt at 165°. On hydrolysis of the ester, the *acid* is obtained in colourless needles which contain H_2O and melt at 233°.

Acetyl-4-methylpyrazolecarboxylic acid is oxidised by potassium permanganate in alkaline solution to *4-methylpyrazoledicarboxylic acid*, $C_3N_2HMe(CO_2H)_2$, which melts at 293°. Distillation of the silver salt in a stream of carbon dioxide yields an oil having the properties of 4-methylpyrazole (Abstr., 1901, i, 167). Ethyl diazoacetate and propionyl acetone yield a pyrazole derivative, $C_{10}H_{11}O_3N_2$, which melts at 59°, and forms an *oxime* and a *semicarbazone*. On hydrolysis, it yields a *ketopyrazolecarboxylic acid* which melts at 191°. G. Y.

Compounds of 1-Phenyl-2:3-dimethyl-5-pyrazolone and its Derivatives with the Methyl Aminohydroxybenzoates.

ALFRED EINHORN (D.R.-P. 126340. Compare Patein and Dufau, Abstr., 1896, i, 188, 650; 1897, i, 375, 543).—*Compounds* having the nature of salts are obtained by melting together 1-phenyl-2:3-dimethyl-5-pyrazolone or one of its homologues and methyl 1:2:4- or 1:2:5-aminohydroxybenzoate. Methyl 1:2:4-aminohydroxybenzoate yields with 1-phenyl-2:3-dimethyl-5-pyrazolone and 1-phenyl-2:3-dimethyl-4-dimethylamino-5-pyrazolone crystalline compounds melting at 82° and 72° respectively. The corresponding ester of the 1:2:5-acid, when combined with these pyrazolone derivatives, gives rise to similar substances melting at 93° and 86° respectively. G. T. M.

[2:6-Dinitro-4-chloro-*pp*-dihydroxydiphenyl-*m*-phenylene Diamine.]

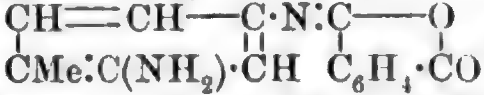
BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 127441).—2:6-*Dinitro-4-chlorodi*-p-*hydroxydiphenyl*-m-*phenylenediamine*,

$$C_6HCl(NO_2)_2(NH\cdot C_6H_4\cdot OH)_2,$$

prepared by heating together 1:2:4-trichloro-3:5-dinitrobenzene, *p*-aminophenol hydrochloride and crystallised sodium acetate in alcoholic solution first at 40° and finally at the boiling point, separates from alcohol as an orange-coloured, crystalline powder which sinters at 155° and decomposes at 215°. It is soluble in alcohol and in sodium hydroxide solution. G. T. M.

[Phthalyltolylenediamines.]

J. R. GEIGY & Co. (D.R.-P. 126964. Compare Biedermann, Abstr., 1877, ii, 783).—The 4-monophthalyl derivative (m. p. 192°) obtained by heating equivalent proportions of phthalic anhydride and 2:4-tolylenediamine probably has the constitution indicated by the formula



$$\begin{array}{l}CH{=\!=}CH{-\!-}C\cdot N{:}C{-\!-}O\\ \quad|\qquad\qquad\quad\ \|\qquad\ |\qquad\ \ |\\ CMe{:}C(NH_2)\cdot CH\ \ C_6H_4\cdot CO\end{array};$$

it is also prepared by condensing *o*-nitro-*p*-toluidine with phthalic anhydride and reducing the *monophthalyl* derivative,

$$NO_2\cdot C_6H_3Me\cdot N{:}C_8H_4O_2.$$

This nitro-compound crystallises from glacial acetic acid in silky needles, and melts at 222°; its isomeride derived from *p*-nitro-*o*-toluidine melts at 232° and yields the isomeric *2-monophthalyl-2:4-tolylenediamine*, a colourless substance melting at 168°.

Both these monophthalyl derivatives, on further treatment with phthalic anhydride, yield the diphthalyl compound melting at 232°.

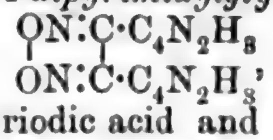
G. T. M.

Electrolytic Reduction of Oximes and Phenylhydrazones in Sulphuric Acid. By Julius Tafel and Ephraim Pfeffermann (*Ber.*, 1902, **35**, 1510—1518. Compare Abstr., 1894, i, 579).—Ethylidenephenylhydrazine, when reduced at 0—4° in 50 per cent. sulphuric acid by a current of 120 amperes, gives rise to a mixture of ethylamine and aniline. Acetonephenylhydrazone, under these conditions, yields aniline and *iso*propylamine. Benzylidenephenylhydrazone, when dissolved in a mixture of dilute sulphuric and acetic acids, furnishes, on electrolysis, benzylamine, benzylaniline, and aniline.

The electrolysis of acetoxime and benzaldoxime leads to the production of *iso*propylamine and benzylamine respectively, the yields of these derivatives being about two-thirds of the theoretical. Acetophenoneoxime and benzophenoneoxime yield *a*-phenylethylamine and benzhydrylamine respectively. Camphoroxime gives rise to bornylamine. Glyoxime, on electrolysis, is decomposed into ammonia and glyoxal; methylglyoxime, under similar conditions, does not yield any diamine, the only base isolated from the product being ammonia.

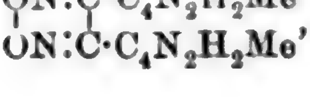
G. T. M.

The Methylated Pyrimidines. By Siegmund Gabriel and James Colman (*Ber.*, 1902, **35**, 1569—1575).—I. Derivatives of 4-methylpyrimidine.—2 : 6-Dichloro-4-methylpyrimidine is converted by chlorine into a mixture of the tetra- and penta-chloro-derivatives. *Pentachloromethylpyrimidine*, $C_5HN_2Cl_5$, crystallises in vitreous prisms or octahedra melting at 82—83°. *Tetrachloroaminomethylpyrimidine*, $C_5HN_2Cl_4{\cdot}NH_2$, is prepared by the action of alcoholic ammonia on the foregoing compound, and crystallises in short prisms, melting and decomposing at 225—227° after sintering at 220°. 5-*Bromo*-2 : 6-*diamino*-4-*methylpyrimidine*, $C_4N_2Me(NH_2)_2Br$, is formed by the action of bromine water on 2 : 6-diamino-4-methylpyrimidine hydrobromide, and crystallises in oblique prisms or rhombohedra, which sinter at 185° and melt and decompose at 188—189°. The substance formed by the action of fuming nitric acid on 4-methylpyrimidine (Abstr., 1900, i, 53) is probably 4 : 4-*dipyrimidylglyoxime peroxide*,



$$\begin{array}{l} \text{ON:C}{\cdot}C_4N_2H_3 \\ \text{ON:C}{\cdot}C_4N_2H_3 \end{array},$$

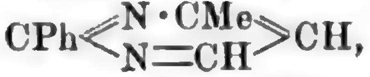
and by reduction with hydriodic acid and phosphonium iodide is converted into the corresponding base, 4 : 4-*dipyrimidylethylenediamine*, $C_4N_2H_3{\cdot}CH(NH_2){\cdot}CH(NH_2){\cdot}C_4N_2H_3$, which crystallises in colourless plates, sinters at 132°, and melts and decomposes at 142—145°. The *hydriodide*, $C_{10}H_{12}N_6,4HI$, forms lemon-yellow, pointed plates, and the *hydrochloride*, $C_{10}H_{12}N_6,4HCl$, forms colourless needles. The *diacetyl* derivative, $C_{10}H_{10}N_6Ac_2$, crystallises in flat needles and melts at 255°.

II. Derivatives of 2 : 4-dimethylpyrimidine.—This compound is converted by nitric acid into *dimethylpyrimidylglyoxime peroxide*,  $\begin{array}{l} \text{ON:C}{\cdot}C_4N_2H_2Me \\ \text{ON:C}{\cdot}C_4N_2H_2Me \end{array}$, which crystallises in rhombic tablets, sinters at

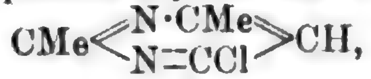
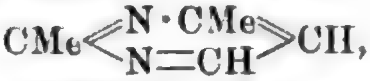
132°, and melts at 134—135°. The *platinichloride* is a yellow, crystalline powder, which does not melt below 270°. The corresponding base, *dimethylpyrimidylethylenediamine*, crystallises in needles, sinters at 158°, and melts and decomposes at 161°; the *hydriodide* crystallises in rhombic plates. The base is accompanied by a substance of lower melting point, the nature of which has not yet been ascertained.

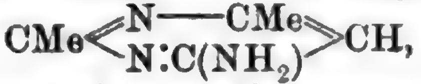
A. H.

The Methylated Pyrimidines. By K. F. M. Julius Schmidt (*Ber.*, 1902, **35**, 1575—1579).—2-*Phenyl*-4-*methylpyrimidine*,



$$\mathrm{CPh}\left\langle\begin{array}{l}\mathrm{N\cdot CMe}\\ \mathrm{N{=}CH}\end{array}\right\rangle\mathrm{CH},$$

is prepared by the reduction of 4:6-chloro-2-phenyl-4-methylpyrimidine, and is a refractive liquid which boils at 279° and solidifies in small prisms melting at 22·5° The *platinichloride* forms yellow spheroids, the *nitrate* melts at 113°, and the *picrate* crystallises from alcohol. 6-*Chloro*-2:4-*dimethylpyrimidine*,  $\mathrm{CMe}\left\langle\begin{array}{l}\mathrm{N\cdot CMe}\\ \mathrm{N{=}CCl}\end{array}\right\rangle\mathrm{CH}$, is prepared by the action of phosphorus oxychloride on hydroxydimethylpyrimidine, and is an oil which boils at 182° and solidifies at 7°. On reduction, it yields 2:4-*dimethylpyrimidine*,  $\mathrm{CMe}\left\langle\begin{array}{l}\mathrm{N\cdot CMe}\\ \mathrm{N{=}CH}\end{array}\right\rangle\mathrm{CH}$, which boils at 146° and has the sp. gr. 1·168 at 13·8°/16°. The base has an odour like that of acetamide and yields crystalline double salts with the usual reagents. 6-*Amino*-2:4-*dimethylpyrimidine*,

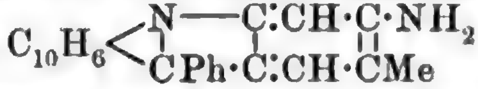


$$\mathrm{CMe}\left\langle\begin{array}{l}\mathrm{N{-\!\!-}CMe}\\ \mathrm{N{:}C(NH_2)}\end{array}\right\rangle\mathrm{CH},$$

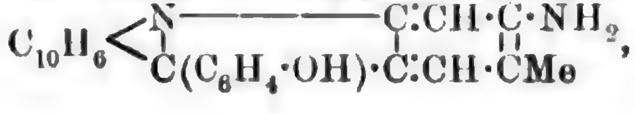
is obtained by the action of alcoholic ammonia on 6-chloro-2:4-dimethylpyrimidine and crystallises in fan-shaped aggregates of needles melting at 183°. The *platinichloride* forms yellow needles, the *picrate* melts at 214°, and the *mercurichloride* forms slender needles. 6-*Anilino*-2:4-*dimethylpyrimidine* melts at 104° and is a mono-acid base.

6-*Thiol*-2:4-*dimethylpyrimidine*, $C_4N_2HMe_2{\cdot}SH$, is prepared by the action of alcoholic potassium hydrosulphide on the chloro-compound and forms yellow crystals which become brown at 225° and melt at 230°. The corresponding *disulphide*, $S_2(C_4N_2HMe_2)_2$, crystallises in short needles melting at 99°. As a rule, the disulphides in the pyrimidine series melt at lower temperatures than the mercaptans.

A. H.

Naphthacridine Colouring Matters. Fritz Ullmann (D.R.-P. 127586. Compare this vol., i, 55, 56, 183).—2-Amino-5-phenyl-3-methylpheno-αβ-naphthacridine,  $C_{10}H_6\left\langle\begin{array}{l}\mathrm{N{-\!\!-}C{:}CH{\cdot}C{\cdot}NH_2}\\ \mathrm{CPh{\cdot}C{:}CH{\cdot}CMe}\end{array}\right.$, is prepared either by heating benzylidene-2:4-tolylenediamine with β-naphthol or by fusing a mixture of benzaldehyde, β-naphthol, and the diamine at 180—190°. If the three nitrobenzaldehydes are employed in this condensation, the corresponding nitroacridine bases are produced.

5-p-*Hydroxyphenyl*-2-*amino*-3-*methylpheno*-αβ-*naphthacridine*,

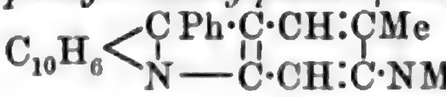


$$C_{10}H_6\left\langle\begin{array}{l}\mathrm{N{-\!\!-\!\!-\!\!-}C{:}CH{\cdot}C{\cdot}NH_2}\\ \mathrm{C(C_6H_4{\cdot}OH){\cdot}C{:}CH{\cdot}CMe}\end{array}\right.,$$

is a sparingly soluble, yellow powder formed by the interaction of *m*-tolylenediamine, *p*-hydroxybenzaldehyde, and β-naphthol. Similar acridine derivatives are obtained by employing *p*-chlorobenzaldehyde and β-hydroxy-α-naphthaldehyde, the product from the latter crystallising in yellow needles melting at 220°. G. T. M.

Naphthacridine Colouring Matters. FRITZ ULLMANN (D.R.-P. 128754. Compare this vol., i, 240).—Naphthacridine derivatives are obtained by heating together β-naphthol and the benzylidene derivatives of the monoalkyl or the *as*-dialkyl-*m*-diamines.

2-Dimethylamino-5-phenyl-3-methylpheno-αβ-naphthacridine,



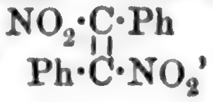
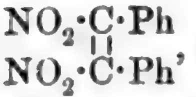
$$C_{10}H_6<\begin{array}{l}C\,Ph\cdot C\cdot CH:CMe\\ N\text{---}C\cdot CH:C\cdot NMe_2\end{array},$$

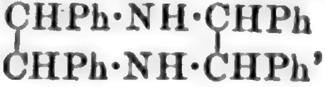
is prepared by condensing together 2-ethyl-*m*-tolylenediamine, benzaldehyde, and β-naphthol at 180—200°.

Similar bases are produced from 2-methyl-*m*-tolylenediamine, *as*-dimethyl-*m*-tolylenediamine, and the corresponding derivatives of *m*-phenylenediamine.

*2-Benzyl-*m*-tolylenediamine,* which also yields an acridine derivative, is prepared from benzyl-4-nitro-*o*-toluidine (m. p. 1·24°); it crystallises from water in sparingly soluble, white needles and melts at 62°.

The properties of the acridine bases are tabulated. G. T. M.

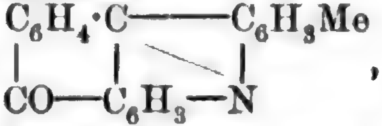
2 : 3 : 5 : 6-Tetraphenyl-*s*-piperazine. JULIUS SCHMIDT (D.R.-P. 126798).—s-α-*Dinitrodiphenylethylene,*  $\begin{array}{l}NO_2\cdot C\cdot Ph\\ Ph\cdot C\cdot NO_2\end{array}$, and its *β-isomeride,*  $\begin{array}{l}NO_2\cdot C\cdot Ph\\ NO_2\cdot C\cdot Ph\end{array}$, produced by passing nitrous fumes into an ethereal solution of tolane, melt respectively at 186—187° and 105—107° (compare Sudborough, Trans., 1897, 71, 223); the α-compound is much less soluble than its isomeride in the ordinary solvents. s-*Dinitrodiphenylethane,* produced by passing nitrogen tetroxide into a benzene solution of stilbene, crystallises in white, silky needles and melts at 235—236°; it may also be prepared by passing nitrous fumes into an ethereal solution of stilbene and decomposing the stilbene nitrosite (m. p. 195—197°) thus obtained by boiling with glacial acetic acid.

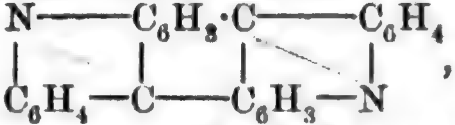
2 : 3 : 5 : 6-*Tetraphenylpiperazine,*  $\begin{array}{l}CHPh\cdot NH\cdot CHPh\\ CHPh\cdot NH\cdot CHPh\end{array}$, is obtained as *hydrochloride* by reducing the preceding compound or either of the *s*-dinitrodiphenylethylenes with zinc dust and glacial acetic acid, rendering the mixture alkaline, extracting with ether, distilling off the solvent, evaporating down the hydrochloric acid solution of the residue, and finally recrystallising the product from the concentrated acid. The hydrochloride crystallises in white needles melting at 254—256°, the platinichloride forms golden-yellow leaflets melting at 204°. The base is a dark yellow oil which partially solidifies; it probably consists of a mixture of isomerides.

The mother liquors from the hydrochloride just described contains the hydrochloride of a stereoisomeric base which melts at 230°.

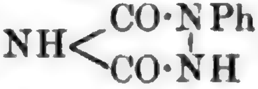
G. T. M.

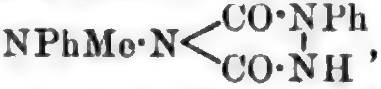
Conversion of 1-Arylaminoanthraquinones into Acridine Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 126444).—Acridine derivatives are produced from the 1-arylaminoanthraquinones by condensing these substances in the presence of dehydrating agents.

The *base*, , prepared by heating at 150° a mixture of 1-*p*-toluidinoanthraquinone and 70 per cent. sulphuric acid, crystallises from dilute alcohol in yellowish-brown needles; its sulphonic acid, obtained from 1-*p*-toluidinoanthraquinonesulphonic acid, is a soluble substance separating in brick-red crystals and dyeing unmordanted wool. The corresponding *base* from 1-anilinoanthraquinone crystallises in golden-yellow leaflets.

The *diamine*, , prepared from 1 : 5-dianilinoanthraquinone separates in dark blue crystals; its dimethyl homologues obtained from 1 : 5- and 1 : 4-di-*p*-toluidinoanthraquinones form dark blue and dark red crystals respectively. Other complex acridine bases of this type are described in the patent, the properties of the whole group being exhibited in tabular form. G. T. M.

Constitution of the Urazoles. By MAX BUSCH (*Ber.*, 1902, 35, 1562—1565. Compare this vol., i, 321).—1-Phenylurazole is converted by ethyl iodide and alcoholic potash into 1-*phenyl*-2 : 4-*dimethylurazole*, which forms large, colourless crystals melting at 93—95°. Both the methyl groups are united with nitrogen, as no methoxyl is found by Zeisel's test. When boiled with dilute aqueous soda, 1-*phenyl*-2 : 4-*dimethylsemicarbazide*, NHPh·NMe·CO·NHMe, is formed and crystallises in snow-white needles melting at 135—136°; a small amount of 1-phenyl-2-methylurazole is also produced.

The constitution of phenyldimethylurazole renders it probable that phenylurazole has the formula  $\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{CO\cdot NH}\end{matrix}$ and does not contain the hydroxyl group as supposed by Acree (this vol., i, 242). A. H.

Herzig and Meyer's Method of Estimating Methyl. By MAX BUSCH (*Ber.*, 1902, 35, 1565—1567).—1-Phenyl-4-methylanilinourazole,  $\mathrm{NPhMe\cdot N}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{CO\cdot NH}\end{matrix}$, the constitution of which is known from its method of preparation, does not conform to Herzig and Meyer's rule, but yields a portion of its methyl in the form of methyl iodide when boiled with hydriodic acid. This appears to be due to the presence of the neighbouring carbonyl group, since benzoylphenylmethylhydrazine behaves in the same way. On the other hand, acetyl- and benzoyl-methylaniline do not yield any methyl iodide when treated in this way. The production of methyl iodide in these circumstances cannot, therefore, be taken as a conclusive proof of the presence of methoxyl, although its non-production may be taken as a proof of the absence of this group. A. H.

Action of Phenylhydrazine on Acylthiocarbamic and Acyliminothiocarbonic Esters. Pyrro-αβ′-diazole [1 : 2 : 4-Triazole] Derivatives. By Henry L. Wheeler and Alling P. Beardsley (*Amer. Chem. J.*, 1902, **27**, 257—270).—When phenylhydrazine reacts with acylurethanes, condensation occurs between the $\cdot NH_2$ group of the hydrazine and the acyl group of the urethane with the formation of 1 : 3-dialkyl-1 : 2 : 4-triazoles [1 : 3-dialkylpyrrodiazoles]. With acylthiourethanes, on the other hand, the reaction takes place between the $\cdot NH_2$ group of phenylhydrazine and the ester group of the thiourethane, giving rise to the isomeric 1 : 5-dialkyl-1 : 2 : 4-triazoles. This difference in behaviour is explained as due to the tendency of the hydrogen of the $\cdot NH_2$ group in phenylhydrazine to react rather with sulphur than with oxygen; this tendency to react with the groups here concerned may be expressed graphically, thus: $>C\cdot S\cdot R > C{:}S > C{:}O > C\cdot O\cdot R$. The authors have studied the action of phenylhydrazine on the following substances.

Methyl benzoylthiocarbamate, when warmed in alcoholic solution with a mol. proportion of the hydrazine for several hours at 100°, furnishes 3-*hydroxy*-1 : 3-*diphenyl*-1 : 2 : 4-*triazole* identical with that prepared by Young (Trans., 1895, **67**, 1063).

Benzyl benzoyldithiocarbamate reacts with phenylhydrazine in the cold, furnishing 3-*mercapto*-1 : 5-*diphenyl*-1 : 2 : 4-*triazole*, which crystallises from alcohol in fine, colourless needles soluble in hot benzene and melting at 187—187·5°. When heated with aniline in sealed tubes at 270—300° for 12 hours, it furnishes the corresponding *monosulphide*, $S(C_{14}H_{10}N_3)_2$, which forms pinkish-brown needles melting at 198°. The *disulphide*, formed when the mercaptotriazole is treated with sodium ethoxide and iodine in alcohol, crystallises in colourless pyramids or arrow-head shaped crystals melting at 174°. The *benzoyl* derivative forms colourless needles melting at 138·5°. The *methyl ether* is produced by the action of methyl iodide on the mercaptotriazole, and crystallises from alcohol in colourless tablets or hexagonal plates meltat 102—103°. The *ethyl ether* forms colourless prisms melting at 97°. The condensation product with ethyl acetate consists of colourless prisms melting at 67°, and the *benzyl ether* crystallises from alcohol in spherical clusters of flattened, colourless prisms melting at 100—100·5°. The constitution of the triazole was ascertained by its synthesis from phenylthiosemicarbazide and benzaldehyde by the action of ferric chloride.

Ethyl benzoyldithiocarbamate reacts in the cold with phenylhydrazine in alcoholic solution, forming mercaptan and *benzoylphenylthiosemicarbazide*. The latter crystallises from alcohol in colourless, six-sided plates or tablets, or when suddenly cooled in long, slender prisms melting at 136—137°. When heated alone or with a little phenylhydrazine, or even by solution in alkali and reprecipitation with hydrochloric acid, it is converted into the 3-mercapto-1 : 5-diphenyl-1 : 2 : 4-triazole already described.

Dibenzoylimidothiobenzylethyleneether, $C_2H_4[S\cdot C(S\cdot CH_2Ph){:}N\cdot COPh]_2$, prepared by the action of ethylene bromide on benzoyldithiobenzylcarbamate in presence of sodium ethoxide, crystallises from alcohol in fine needles, colourless, but with a faint green tinge, melting at 93·5—94°, and reacts with phenylhydrazine to form the 3-benzylmercapto-1 : 5-diphenyltriazole already described.

The *ethyl acetate* derivative of *acetyldithiocarbamic acid*,

$$\mathrm{COMe\cdot NH\cdot CS\cdot S\cdot CH_2\cdot CO_2Et},$$

prepared by warming ethyl thiocyanoacetate with thioacetic acid, forms yellow needles or slender prisms from benzene or light petroleum and melts at 82°. When heated with phenylhydrazine for several hours at 100°, it forms *3-mercapto-1-phenyl-5-methyl-1 : 2 : 4-triazole*, which crystallises from alcohol in colourless prisms melting at 163—164°.

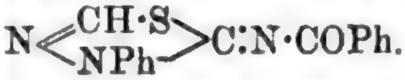
Ethyl benzoyliminomonothiocarbonate, $\mathrm{COPh\cdot N{:}C(SEt)\cdot OEt}$, reacts with phenylhydrazine in benzene solution at the atmospheric temperature, and after a few hours radiating groups of colourless needles melting at 136° separate of *benzoyl-ψ-ethylphenylsemicarbazide*,

$$\mathrm{COPh\cdot NH\cdot C(OEt){:}N\cdot NH\cdot Ph},$$

which, when heated in alcoholic solution with phenylhydrazine, is converted into 3-ethoxy-1 : 5-diphenyl-1 : 2 : 4-triazole (Young, *loc. cit*).

n-Propyl benzoyldithiocarbamate reacts with *p*-tolylhydrazine to form *3-mercapto-5-phenyl-1-*p*-tolyl-1 : 2 : 4-triazole*, which crystallises from alcohol in needles or prisms melting at 168°.

5-Mercapto-1 : 3-diphenyl-1 : 2 : 4-triazole, obtained by the interaction of formylphenylhydrazine with benzoyl thiocyanate, crystallises from alcohol in white, hair-like needles which sinter and melt at about 248—249°. A second substance, insoluble in alkalis, is formed in this reaction, which crystallises from alcohol in slender prisms or needles melting at 119—120°. When heated with dilute alkalis, it dissolves with the formation of aniline or phenylhydrazine and a benzoate, whence the authors conclude that it is probably *1-benzoylimino-2-phenylthiodiazoline*,

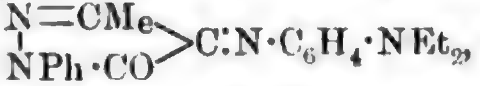


$$\mathrm{N}{<}\begin{matrix}\mathrm{CH\cdot S}\\ \mathrm{NPh}\end{matrix}{>}\mathrm{C{:}N\cdot COPh}.$$

aa-Carbethoxyphenylsemicarbazide, resulting from the interaction of phenylsemicarbazide with ethyl chlorocarbonate at 100°, crystallises from a mixture of alcohol and benzene in bunches of fine, hair-like needles, melts at 171·5°, and dissolves readily in alcohol, but only sparingly in benzene. With sodium hydroxide, sodium ethoxide, or acetyl chloride it furnishes phenylurazole, and is apparently identical with the supposed dicarbethoxyphenylsemicarbazide described by Acree (Abstr., 1902, i, 242). T. A. H.

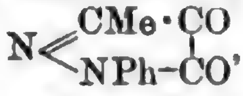
as-o-Diaminodibenzylhydrazine. By Theo Ulmer (*Ber.*, 1902, **35**, 1567—1569).—When dinitrodibenzylnitrosoamine is reduced at 15° by zinc dust in presence of alcoholic acetic acid, it yields *diaminodibenzylhydrazine hydrochloride*, which crystallises in small, colourless plates melting above 260°. The free *base*, $\mathrm{NH_2\cdot N(CH_2\cdot C_6H_4\cdot NH_2)_2}$, forms soft, white needles melting indefinitely at 64—65°. It decomposes rapidly on preservation, but has all the properties of a hydrazine and yields with acetic anhydride the triacetyl derivative previously described by Busch and Weiss (Abstr., 1900, i, 699). A. H.

Ketopyrazolone. I. By Franz Sachs and Hermann Barschall (*Ber.*, 1902, **35**, 1437—1439. Compare Pschorr, *Inaug. Diss. Jena*, 1894; Knorr, Abstr., 1887, 601).—*p*-Nitrosodiethylaniline condenses with 1-phenyl-3-methylpyrazolone to form the *compound*



$$\begin{matrix} N{=}CMe \\ | \\ NPh{\cdot}CO \end{matrix}\!\!>\!C{:}N{\cdot}C_6H_4{\cdot}NEt_2,$$

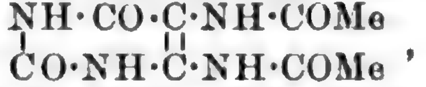
which forms large, dark green glistening crystals and melts at 117°. The corresponding *dimethylamino*-compound separates from alcohol in small, dark green crystals, melts at 187°, and is less soluble than the diethyl compound. Both compounds are hydrolysed by mineral acids to a diamine base and 1-*phenyl*-3-*methylketopyrazolone*,



$$N\!\!<\!\!\begin{matrix} CMe{\cdot}CO \\ \quad\;| \\ NPh{-}CO \end{matrix},$$

the isatine of the series, which sublimes, or separates from light petroleum, in bronze-coloured, glistening crystals and melts at 119°. The hydrate melts at 71°, the oxime at 157°, and the phenylhydrazone at 155° (Pschorr, *loc. cit.*). The diketone condenses with *o*-phenylenediamine to a cinnabar-red *azine* which melts at 225°. T. M. L.

4 : 5-Diacetyldiaminouracil. C. F. Boehringer & Söhne (D.R.-P. 126797. Compare this vol., i, 125).—4 : 5-*Diacetyldiaminouracil* (4 : 5-*diacetyldiamino*-2 : 6-*dioxydihydropyrimidine*),



$$\begin{matrix} NH{\cdot}CO{\cdot}C{\cdot}NH{\cdot}COMe \\ |\qquad\quad\;\, \| \\ CO{\cdot}NH{\cdot}C{\cdot}NH{\cdot}COMe \end{matrix},$$

produced together with 8-methylxanthine by condensing uric acid with acetic anhydride in the presence of pyridine, quinoline, or dimethylaniline, crystallises from water in felted aggregates of slender needles, sinters at 300°, and decomposes at higher temperatures; it reduces ammoniacal silver nitrate on prolonged boiling, gives the murexide coloration with concentrated hydrochloric acid, and is hydrolysed to monoacetyldiaminouracil, $C_6H_8O_3N_4$, by alkali hydroxides. A *triacetyl* derivative, $C_{10}H_{12}O_5N_4$, is also formed in the condensation, but is hydrolysed to the diacetyl compound by the action of water; the total yield of the latter substance is 75 per cent. of the uric acid employed. G. T. M.

Homologues of Xanthine. C. F. Boehringer & Söhne (D.R.-P. 128212).—1 : 3 : 7 : 8-*Tetramethylxanthine* (8-*methylcaffeine*), prepared by heating 8-methylxanthine, 3 : 8-dimethylxanthine, or 1 : 3 : 8-trimethylxanthine with methyl iodide and 2*N*-sodium or potassium hydroxide solution for 4 to 7 hours at 80°, crystallises from water or the ordinary organic solvents in concentric aggregates of lustrous needles sintering at 205° and melting at 207—208·5°; at higher temperatures, it volatilises without decomposition.

3 : 7 : 8-*Trimethylxanthine*, produced by heating the dry barium, lead, or dipotassium derivative of 8-methylxanthine with an ethereal solution of methyl iodide at 120—123° for 60 hours, crystallises from water in lustrous needles and from alcohol in short, thick prisms; it dissolves in acid and alkali solutions, and yields a *sodium* derivative separating in slender, felted needles. The base sinters at 296° and melts at 302—303°; it sublimes without decomposition.

7-*Benzyl*-1 : 3 : 8-*trimethylxanthine*, obtained by the action of benzyl chloride and alcoholic sodium hydroxide solution on 1 : 3 : 8-trimethylxanthine, crystallises in clusters of needles melting at 159—160·5°.

8-*Methyl*-1 : 3 : 7-*triethylxanthine*, prepared from 8-methylxanthine by the action of ethyl iodide and sodium hydroxide, crystallises in vitreous prisms sintering at 128° and melting at 132—133°.

1 : 3 : 7-*Trimethyl*-8-*ethylxanthine* forms needles melting at 186—187·5° ; *triethylxanthine* separates in hexagonal plates, sintering at 195° and melting at 210—212°. G. T. M.

Thioxanthine. C. F. Boehringer & Söhne (D.R.-P. 128117. Compare Abstr., 1898, i, 340).—Thioxanthine (2 : 6-dioxy-8-thiopurine) may be prepared by heating the alkali urates in aqueous solution or suspension with carbon disulphide at 150°. G. T. M.

Synthesis of Methylrubazonic Acid. By Fr. Pröscher (*Ber.*, 1902, **35**, 1436—1437.)—Methylrubazonic acid can be prepared by the condensation of nitrosoantipyrine with phenylmethylpyrazolone. Nitrosoantipyrine also condenses with pyrrole and other bases to form indamine dyes. T. M. L.

Spontaneous Decomposition of Nitrosobenzene. By Eugen Bamberger (*Ber.*, 1902, **35**, 1606—1614).—When nitrosobenzene in solution in dry benzene is exposed to sunlight, it rapidly decomposes, forming mainly azoxybenzene, together with small quantities of nitrobenzene, aniline, *o*-hydroxyazobenzene and *o*-hydroxyazoxybenzene, and traces of quinol, *iso-o*-hydroxyazoxybenzene, *p*-hydroxyazoxybenzene, and other substances. The same decomposition takes place, only far more slowly, in the absence of light. When heated alone or in solution in petroleum, nitrosobenzene yields the same products. With the exception of quinol, the substances just mentioned are obtained by the action of sodium hydroxide on nitrosobenzene (Abstr., 1900, i, 531) and are separated in the manner previously described.

The opinion is expressed that in this decomposition nitrosobenzene is first converted into a mixture of phenylhydroxylamine and nitrobenzene; the former then, with unchanged nitrosobenzene, yields azoxybenzene. On the other hand, phenylhydroxylamine, under the same conditions, forms nitrosobenzene and aniline, the former with unchanged phenylhydroxylamine producing azoxybenzene (Abstr., 1900, i, 221). K. J. P. O.

Hydroxyazoxybenzenes. By Eugen Bamberger (*Ber.*, 1902, **35**, 1614—1623).—An investigation of *o*-hydroxyazoxybenzene (m. p. 75·5—76°) and *iso-o*-hydroxyazoxybenzene (m. p. 108—108·5°) (Abstr., 1900, i, 531) has shown that they both have a mol. weight, represented by the formula $C_{12}H_{10}O_2N_2$; both dissolve in aqueous sodium hydroxide, are reduced by zinc and ammonium chloride to a mixture of *o*-aminophenol and aniline, and by concentrated sulphuric acid are converted into *o*-hydroxyazobenzene.

o-*Acetoxyazoxybenzene*, $C_6H_5{\cdot}N_2O{\cdot}C_6H_4{\cdot}OAc$, prepared from acetic anhydride and *o*-hydroxyazoxybenzene, crystallises in lustrous, straw-yellow prisms melting at 56—57° ; the acetyl derivative of the *iso*-compound was not obtained in a pure state.

Benzeneazo-o-*hydroxyazoxybenzene*, $N_2Ph{\cdot}C_6H_3(OH){\cdot}N_2O{\cdot}Ph$, is formed by the action of benzenediazonium acetate on *o*-hydroxyazoxybenzene or on the *iso*-compound (?); it crystallises in pale orange-yellow needles melting at 145—145·5°, and dissolves in alkali hydroxides with a bordeaux-red coloration. It is thought that these two substances are possibly stereoisomeric.

The *p*-hydroxyazoxybenzene (m. p. 145°) obtained by Kekulé and Hidegh (*Ber.*, 1870, **3**, 235) by the action of phosphorus pentachloride on *p*-hydroxyazobenzene, is not identical with the compound (m. p. 156—156·5°) prepared from nitrosobenzene by the author (*loc. cit.*). As Kekulé and Hidegh's substance is not soluble in alkali hydroxides and is not oxidised by permanganate, it does not bear the same relation to the author's *p*-hydroxyazoxybenzene that *o*-hydroxyazoxybenzene bears to *iso-o*-hydroxyazoxybenzene. K. J. P. O.

Synthesis of *p*-Hydroxyazoxybenzene. By EUGEN BAMBERGER and WALTHER BERNAYS (*Ber.*, 1902, **35**, 1624—1626. Compare preceding abstracts).—*p*-Hydroxyazoxybenzene was synthesised by condensing phenylhydroxylamine and *p*-nitrosophenol, and was identical with the substance previously obtained by the decomposition of nitrosobenzene (Abstr., 1900, i, 531). The yield of *p*-hydroxyazoxybenzene was very small; purification was only effected by repeated fractional precipitation of the ammoniacal solution with carbon dioxide. K. J. P. O.

Reduction Products of the Nitronaphthalenes. By LEONHARD WACKER (*Annalen*, 1902, **321**, 61—70. Compare Abstr., 1901, i, 655).—α-Nitronaphthalene, when reduced either with dextrose or phenylhydrazine and alcoholic sodium hydroxide solution, yields a yellow compound melting at 120°, and probably having the formula $C_{20}H_{12}ON_2$. 5 : 5′-*Dinitroazoxynaphthalene*, $ON_2(C_{10}H_6 \cdot NO_2)_2$, obtained by reducing 1 : 5-dinitronaphthalene with zinc dust and ammonium chloride or phenylhydrazine and sodium hydroxide, is orange-yellow and decomposes above 200°. 1 : 1′-Azoxynaphthalene-5 : 5′-disulphonic acid is readily obtained from sodium 1 : 5-nitronaphthalenesulphonate by reduction with dextrose and aqueous sodium hydroxide solution; it is isolated in the form of its *sodium* salt, $C_{20}H_{12}O_7N_2S_2Na_2,2H_2O$, which crystallises from water in prisms or leaflets. *Hydroxyazonaphthalene*-5 : 5′-*disulphonic acid*, produced by dissolving the preceding sodium salt in 90—93 per cent. sulphuric acid at 35°, is isolated as the *ammonium* salt, $C_{20}H_{20}O_7N_4S_2$. *Azoxynaphthalene*-3 : 8 : 3′ : 8′-*tetrasulphonic acid*, prepared by reducing sodium α-nitronaphthalene-3 : 8-disulphonate with dextrose and aqueous sodium hydroxide solution at 50°, is obtained in the form of its yellow *potassium* salt, $ON_2[C_{10}H_5(SO_3K)_2]_2$, this substance separating from aqueous solutions of the acid on adding excess of potassium hydroxide. This azoxynaphthalenetetrasulphonic acid is not readily transformed into a hydroxyazo-compound, but the sulphonic acids of α-nitronaphthalene containing the sulphonic acid groups in positions 6, 7, and 8 are readily reduced, and easily undergo this transformation. G. T. M.

Action of the Malonic Esters on Diazonium and Tetrazonium Chlorides. By G. FAVREL (*Bull. Soc. Chim.*, 1902, [iii], **27**, 313—323).—By the action of ethyl malonate on diphenyltetrazonium chloride in acetic acid solution, *ethyl diphenyldihyrazonemalonate*, $C_{12}H_8[NH·N:C(CO_2Et)_2]_2$, is obtained, which crystallises in small, lustrous, yellow plates melting at 178—180°; it readily dissolves in alcohol, benzene, toluene, xylene, nitrobenzene, or aniline, but is insoluble in aqueous or alcoholic solutions of the alkalis. When acted on by sodium ethoxide, the *disodium* derivative is obtained as a reddish, crystalline powder; when this is acted on by alkyl iodides or by acyl chlorides, no alkyl or acyl derivatives of ethyl diphenyldihydrazonemalonate are obtained. *Diphenyldihydrazonemalonic acid* is a clear yellow powder insoluble in the ordinary solvents in the cold; on warming, it decomposes; it has not been found possible to prepare the hexa-sodium derivative of the acid. *Methyl diphenyldihydrazonemalonate*, obtained in a similar manner to the ethyl ester, forms small, yellow crystals which melt at 217—220°; it is insoluble in alcohol or ether. *Ethyl di-o-tolyldihydrazonemalonate*, obtained from ethyl malonate and ditolyltetrazonium chloride, forms small, orange-red crystals which melt at 188—190°, and are sparingly soluble in alcohol, but much more so in toluene, xylene, nitrobenzene, aniline, chloroform, or acetone. Its disodium derivative forms small red crystals. *Di-o-tolyldihydrazonemalonic acid* is much more stable than diphenyldihydrazonemalonic acid, and can be obtained in small, orange-coloured plates which decompose without melting at 195—200°. The *methyl* ester of this acid crystallises from nitrobenzene in bundles of small, reddish crystals which melt at 210—212°. *Ethyl di-o-anisyldihydrazonemalonate* forms orange-coloured crystals melting at 190—192°, the *methyl* ester separates from hot aniline in yellow crystals which melt at 268—270°.

The foregoing compounds are probably all to be regarded as dihydrazones of mesoxalic acid or its esters (compare Meyer, Abstr., 1891, 922). A. F.

Action of Substituted Malonic Esters on Diazonium Chlorides. By G. Favrel (*Bull. Soc. Chim.* 1902, [iii], **27**, 324—328).—By the action of diazonium chlorides on substituted malonic esters, hydrazones of ketonic acids are obtained, with production of alcohol and elimination of carbon dioxide. In this way, the author has prepared the phenylhydrazone and *p*-tolylhydrazone of ethyl pyruvate, and the phenylhydrazone and the *o*-tolylhydrazone of α-ketobutyric acid, the latter compound melting at 156°. A. F.

Action of Acetylacetone and of its Substituted Derivatives on Diazonium and Tetrazonium Chlorides. By G. Favrel (*Bull. Soc. Chim.*, 1902, [iii], **27**, 328—336).—By the action of diphenyltetrazonium chloride on acetylacetone, there is obtained *acetylacetone diphenyldihydrazone* (*βδ-pentanedione-γ-diphenyldihydrazone*, $CAc_2:N·NH·C_6H_4·C_6H_4·NH·N:CAc_2$; it is insoluble in the ordinary solvents but dissolves in boiling aniline or nitrobenzene, from which it separates in small, reddish crystals melting at 258—260°. It is very stable, and is decomposed only by fusing with alkali hydroxides; it does not react with phenylhydrazine. Its *sodium* derivative crystallises from acetone or pyridine in small, reddish crystals.

If mol. proportions of acetylacetone and diphenyltetrazonium chloride are allowed to interact in acetic acid solution, a substance which is probably cyclo*diphenylformazyl methyl ketone*, is produced.

Acetylacetonediphenyldimethylhydrazone (*βδ-pentanedione-γ-diphenyldimethylhydrazone*), obtained by the action of methyl sulphate on sodioacetylacetonediphenyldihydrazone, separates from its alcoholic solution in small, reddish crystals which melt at 168—170°.

Acetylacetonedi-o-tolyldihydrazone (*βδ-pentanedione-γ-di-o-tolyldihydrazone*), obtained in a similar manner to the preceding analogous compounds, forms small, red needles which melt at 250—252°, and are insoluble in the ordinary solvents but soluble in hot aniline or nitrobenzene. Its *disodium* derivative forms small, red, lamellar crystals, insoluble in water or alcohol, soluble in acetone or in pyridine.

Acetylacetonedi-o-tolyldimethylhydrazone (*βδ-pentanedionedi-o-tolyldimethylhydrazone*), obtained by heating the preceding disodium compound with methyl sulphate, forms small, red, silky crystals melting at 247—248°.

Acetylacetonedi-o-anisyldihydrazone (*βδ-pentanedione-γ-di-o-anisyldihydrazone*), forms slender, scarlet-coloured needles which melt at 234—235°. *Sodioacetylacetonedi-o-anisyldihydrazone* crystallises from pyridine in very light, small red needles.

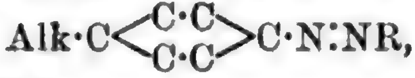
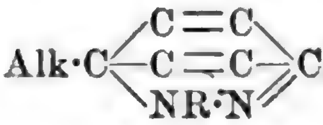
Acetylacetonedi-o-anisyldimethylhydrazone (*βδ-pentanedione-γ-di-o-anisyldimethylhydrazone*), crystallises from chloroform in small, red needles which melt at 257—258°. A. F.

Action of Alkylacetylacetones on Diazonium and Tetrazonium Chlorides. By G. Favrel (*Bull. Soc. Chim.*, 1902, [iii], **27**, 336—342).—By the action of benzenediazonium chloride on methylacetylacetone in acetic acid solution, diacetylmonophenylhydrazone is obtained. Similarly, by the action of *p*-toluenediazonium chloride on methylacetylacetone, there is obtained *diacetylmono-*p*-tolylhydrazone*, which forms small, yellowish crystals melting at 119—120°, and with *o*-toluenediazonium chloride, *diacetylmono-o-tolylhydrazone*, which forms crystals of a clear yellow colour melting at 130—131°.

Further, by adding solutions of diphenyltetrazonium chloride and di-*o*-tolyltetrazonium chloride to alcoholic solutions of methylacetylacetone, *diacetyldiphenyldihydrazone*, melting at 283—284°, and *di-o-tolyldihydrazone*, melting at 240—242° respectively, are obtained.

By acting on ethylacetylacetone with diazonium and tetrazonium chlorides, corresponding derivatives of propionylacetyl are obtained. The *propionylacetylmono-*p*-tolylhydrazone* (*βγ-pentanedione-γ-*p*-tolylhydrazone*) forms small, orange-coloured crystals melting at 137—138°, and *propionylacetylmono-o-tolylhydrazone* (*βγ-pentanedione-γ-o-tolylhydrazone*) forms pale yellow coloured crystals melting at 58—60°. *Propionylacetyldiphenyldihydrazone* (*βγ-pentanedione-γ-diphenyldihydrazone*), obtained by the action of diphenyltetrazonium chloride on ethylacetylacetone, crystallises from nitrobenzene or aniline in red coloured crystals melting at 292—294°.

A. F.

Action of Hydrazine Bases on "Quinols" [ψ-Quinols]. Notes on the History of "Quinols." By Eugen Bamberger (*Ber.*, 1902, **35**, 1424—1431).—The products obtained by the interaction of ψ-quinols with *p*-nitrophenylhydrazine and with semicarbazide are azo-compounds of the type  $\mathrm{Alk{\cdot}C}{<}\substack{\mathrm{C{\cdot}C}\\ \mathrm{C{\cdot}C}}{>}\mathrm{C{\cdot}N{:}NR}$, instead of being cyclic anhydrides, , as previously considered (Abstr., 1901, i, 140).

The interaction of 1-hydroxy-4-ketotoluene with phenylhydrazine yields *p*-tolueneazobenzene, identical with the substance obtained by the interaction of nitrosobenzene and *p*-toluidine (Mills, Trans., 1895, **67**, 929); the azo-compound melts at 69·5—70·5°, and sublimes between 80° and 90° in orange leaflets. By using *p*-nitrophenylhydrazine, p-*tolueneazo*-p-*nitrobenzene*, $C_6H_4Me{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$, is obtained; it crystallises in red, lustrous, felted needles and melts at 181°.

The interaction of 1-hydroxy-4-ketotoluene with semicarbazide yields p-*tolueneazocarbonamide*, $C_6H_4Me{\cdot}N_2{\cdot}CO{\cdot}NH_2$, which crystallises from water in orange-red leaflets or flat needles with a bronze lustre, melts at 141·5—142°, and can also be obtained by oxidising p-*tolylsemicarbazide*, $C_6H_4Me{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, with aqueous potassium permanganate; the latter is formed by the action of potassium cyanate on *p*-tolylhydrazine in aqueous solution and crystallises in silky, white leaflets or flat needles and melts at 190—191°.

A note as to the history of the "quinols" is appended. W. A. D.

Electrochemical Reduction of 2 : 2′-Dinitrodiphenyl to Phenazone and Derivatives of the Latter. By Th. Wohlfahrt (*J. pr. Chem.*, 1902, [ii], **65**, 295—299).—2 : 2′-Dinitrodiphenyl gives a 95 per cent. yield of phenazone when electrolysed under the following conditions:—anode, lead strips in a cold saturated solution of sodium carbonate; cathode, a cylinder of nickel gauze of 250 sq. cm. area immersed in a solution of 10 grams of the substance in 200 c.c. of alcohol with 30 c.c. of water and 2 grams of sodium acetate and cathode density of 5—6 amperes per sq. dcm.

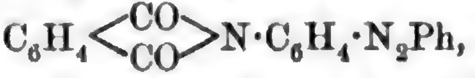
Methylphenazone methyl sulphate, obtained by heating phenazone with an excess of methyl sulphate at 80—100°, separates from alcohol in very hygroscopic, yellow needles, and when heated with potassium iodide, yields *phenazone methiodide* which separates from glacial acetic acid in dark-red crystals, darkens at 100° and melts at 185—187°. *Methylphenazone platinichloride* crystallises in lustrous yellow leaflets.

Phenazone ethiodide, obtained by the action of ethyl iodide on phenazone, separates from an alcoholic solution on the addition of ether and melts at 185—187°. R. H. P.

Compounds of Sodium Tetrazoditolylsulphonate with Aromatic Amines and Phenols, and their Conversion into Azo-colours. By Alphonse Seyewetz and Biot (*Compt. rend.*, 1902, **134**, 1068—1070).—When aqueous solutions of sodium tetrazoditolylsulphonate and an aromatic amine are mixed, colourless, crystalline compounds are produced which become coloured by the action of light or by prolonged boiling with alcohol. Compounds have been obtained from aniline and the toluidines; they decompose at 160°, are little soluble in water or cold alcohol, insoluble in ether, benzene, or chloroform, but easily soluble in hot alcohol. Diamines react precisely in the same way as monoamines, as has been proved with *p*-phenylenediamine. Similar compounds have also been prepared with α- and β-naphthylamine and α-ethylnaphthylamine.

Two molecules of the amine react with one molecule of the tetrazo-compound, and a colourless hydrazine compound is formed. Thus, in the case of naphthylamine (hydrochloride) the reaction is represented: $NaSO_3{\cdot}N{:}N{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}SO_3Na + 2(C_{10}H_7NH_2,HCl) = 2NaCl + NH_2{\cdot}C_{10}H_6{\cdot}N(SO_3H){\cdot}NH{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}NH{\cdot}N(SO_3H){\cdot}C_{10}H_6{\cdot}NH_2$. The coloured substance is produced from this hydrazine derivative according to the equation $C_{34}H_{32}O_6N_6S_2 = 2SO_2 + 2H_2O + NH_2{\cdot}C_{10}H_6{\cdot}N{:}N{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}NH_2$. That the substances contain amino-groups is proved by the fact that they can be diazotised. J. McC.

Derivatives of *p*-Aminoazobenzene. By Maryan Wieleżyński (*Ber.*, 1902, **35**, 1431—1433).

—*Methoxalylaminoazobenzene*, $CO_2Me{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Ph$, obtained by heating methyl oxalate and aminoazobenzene, crystallises from benzene in orange-yellow leaflets and melts at 178—179°. *Succinyl*-p-*aminoazobenzene*, $C_2H_4(CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Ph)_2$, prepared from succinyl chloride and the base, crystallises from amyl acetate and melts at 221—222°. *Benzoyl*-p-*aminoazobenzene* crystallises from glacial acetic acid in golden leaflets and melts at 205°. *Phthalyl*-p-*aminoazobenzene*,  $C_6H_4{<}{}^{CO}_{CO}{>}N{\cdot}C_6H_4{\cdot}N_2Ph$, prepared by using phthalyl chloride, crystallises from glacial acetic acid in flesh-coloured crystals melting at 250°. *Cinnamylidene*-p-*aminoazobenzene*, $CHPh{:}CH{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}N_2Ph$, obtained by means of cinnamaldehyde, crystallises from alcohol in small, orange-yellow crystals and melts at 136°; *vannillylidene*-p-*aminoazobenzene* forms small, dark red crystals and melts at 157°.

Formaldehyde combines with *p*-aminoazobenzene to yield the *derivative*, $CH_2{:}N{\cdot}C_6H_4{\cdot}N_2Ph$, melting at 196—200°, but acetaldehyde, acetone, and œnanthaldehyde are without action. W. A. D.

Conversion of Hydrazobenzene into Benzidine by Glacial Acetic Acid. By Franz Sachs and Croyden M. Whittaker (*Ber.*, 1901, **35**, 1433—1435. Compare Rassow and Rülke, this vol., i, 404).

—The conversion of hydrazobenzene into benzidine can be brought about by organic acids if some substance is present to combine with the benzidine as fast as it is formed. Thus when heated with acetic acid and *p*-dimethylaminobenzaldehyde, hydrazobenzene is completely converted into bis-*p*-dimethylaminobenzylidenebenzidine, $C_{12}H_8(N{:}CH{\cdot}C_6H_4{\cdot}NMe_2)_2$; this base, which has not previously been prepared in a pure state, is a yellow powder which can be crystallised from nitrobenzene and melts at 317°.

By boiling with acetic acid alone, hydrazobenzene was converted into diacetylbenzidine, which melts at 329—331° (corr.) and not at 317°. T. M. L.

Action of Nascent Chlorine on Proteids. By R. EHRENFELD (*Zeit. physiol. Chem.*, 1902, **34**, 566—579. Compare Abstr., 1901, i, 622).—Egg-albumin, serum-albumin, vitellin, legumin, and other proteids react with nascent chlorine in very much the same manner as casein, and the chlorinated products obtained resemble proteids in both physical and chemical properties. When moist, they dissolve in alcohol containing a little hydrochloric acid and in acetic acid, also in alkali hydroxides in aqueous ammonia. The percentage composition of the different products varies considerably. The chlorine derivative from egg-albumin contains 6·51, that from serum-albumin 8·95, that from vitellin 10·0, from legumin 9·63 and from gluten (?) 4·81 per cent. of chlorine, and all appear to be free from sulphur. J. J. S.

Compounds of Proteids with Metaphosphoric Acid. By ERNST FULD (*Beitr. chem. Physiol. Path.*, 1902, **2**, 155—168).—A method is described by means of which compounds of proteid and metaphosphoric acid of constant composition can be prepared. The proteids used were crystallised serum-albumin, crystallised egg-albumin, casein, and edestin. The amount of phosphorus is different in the various proteid meta-phosphates. Of the proteoses, hetero-proteose was the only one which gives a well marked precipitate with metaphosphoric acid. W. D. H.

Formation of Glycogen from Proteid. By ERNST BENDIX (*Zeit. physiol. Chem.*, 1902, **34**, 544—548).—A reply to Schöndorff (this vol., ii, 154). J. J. S.

Pseudo-mucin. By CARL NEUBERG and FELIX HEYMANN (*Beitr. chem. Physiol. Path.*, 1902, **2**, 201—213).—Leathes has shown that by peptic digestion the viscid substance known as paramucin passes into the easily soluble form (pseudo-mucin). Both these ovarian mucoids resemble mucin in their glucoside character. In the true mucins, the reducing material appears to be a substance which yields glucosamine (chitosamine). Concerning the nature of the carbohydrate group in ovarian mucoid, three opinions have been recently expressed. Panzer (Abstr., 1900, i, 70) considers it to be an ethereal sulphate allied to chondroitin-sulphuric acid, which by hydrolysis yields glucosamine and a pentose. Leathes (Abstr., 1900, i, 318) names the reducing material paramucosin; this is regarded as a reduced chondrosin (anhydro-chitosamine-glycuronic acid); on hydrolysis, it yields gulose and chitosamine. Zangerle (*Münch. med. Woch.*, 1900, 214) obtained a crystalline benzoate of an amino-sugar; this benzoate, when hydrolysed, yielded, with hydrochloric acid, a substance crystallographically identified as glucosamine hydrochloride. In the present research, a fourth result is arrived at. Pseudo-mucin was decomposed by fuming hydrobromic acid, and after further treatment a compound of cinchonine was obtained with the composition of cinchonine *nor*isosaccharate. According to Fischer and Tiemann, *nor*isosaccharic acid is only obtainable from chitin and glucosamine. It is therefore proved that pseudo-mucin contains a glucosamine-yielding group in important quantities. No other carbohydrate substance is present. Gulose, which according to Leathes enters into the composition of paramucin, was not found. W. D. H.

Hydrolysis of Gelatin. By EMIL FISCHER, P. A. LEVENE, and R. H. ADERS (*Zeit. physiol. Chem.*, 1902, **35**, 70—79. Compare Abstr., 1901, i, 780).—Gelatin was hydrolysed by heating for several hours with hydrochloric acid, and the amino-acids thus formed converted into esters (Abstr., 1901, i, 192). On saturating the alcoholic solution of the esters with hydrogen chloride, glycine may be completely separated as the hydrochloride of the ester. The esters of the amino-acids contained in the mother liquid are separated by fractionation under a pressure of 8—10 mm.; the first fraction (b. p. 40—55°) contained mainly the ester of *d*-alanine, the second (b. p. 55—80°) that of *l*-pyrrolidine-2-carboxylic acid, the third (80—100°) the ethyl ester of *l*-leucine, together with the last-mentioned ester, the fourth (b. p. 100—130°) ethyl aspartate, together with other substances, the fifth (b. p. 130—160°) the esters of *d*-phenylalanine, and *d*-glutamic acid. On hydrolysing the esters, the active acids were always partially racemised. Glycine represents 16·5 per cent. of the dry gelatin, alanine 0·8, pyrrolidinecarboxylic acid 5·2, leucine 2·1, aspartic acid 0·56, glutamic acid 0·88, and phenylalanine 0·4 per cent. Aminovaleric acid is also probably formed, and possibly aminobutyric acid.
K. J. P. O.

Dissociation and Combination of Witte's Peptone. By TORALD SOLLMANN (*Amer. J. Physiol.*, 1902, **7**, 203—219).—Data are given relating to the reaction of Witte's peptone towards different indicators, the composition of the ash, the dissociability of the pure albumose solution, the combination of Witte's peptone with sulphuric acid, and the combination of albumose with sodium hydroxide. Witte's peptone has an average mol. weight of 630, but is dissociable into four molecules by dilution. By heat, an alkaline molecule is eliminated; it appears to be univalent towards acids or bases. W. D. H.

Hydrolysis of Acid Amides and Anilides by Ferments. By MAX GONNERMANN (*Pflüger's Archiv*, 1902, **89**, 493—516).—Experiments were carried out with the following amides and anilides: formamide, acetamide, oxamide, succinamide, benzamide, salicylamide, formanilide, acetanilide, oxanilide, and benzanilide. Of these, formanilide and acetanilide are hydrolysed by pepsin; acetamide, formanilide, and acetanilide by trypsin; acetamide and formanilide by emulsin. Ptyalin, invertin, and maltin have no action on any of these substances. The finely divided liver of the sheep brings about the hydrolysis of formamide, acetamide, succinamide, benzamide, and formanilide, whilst the finely divided kidneys of the sheep bring about the hydrolysis of formamide, benzamide, salicylamide, formanilide, and benzanilide. The results obtained with these two organs agree with those obtained by various workers in experiments made on living animals. All the experiments were carried out in presence of 1 per cent. of sodium fluoride to prevent bacterial action.

The aqueous solution of acetamide has an acid reaction. Acetamide readily volatilises when its aqueous solution is evaporated. "Pure" oxamide was found in some cases to contain a large amount of oxalic acid. Salicylic acid is readily soluble in concentrated ammonium acetate solution and can thus be separated from the amide, which is insoluble. A. H.

An Important Source of Error in the Examination of Diastases. By M. Emm. Pozzi-Escot (*Compt. rend.*, 1902, **134**, 479—480).—The white, aqueous emulsion of guaiacum resin, when mixed with a few drops of hydrogen peroxide, developed a blue coloration in the presence of oxydases and other diastases. This reaction is, however, by no means general for all classes of diastases.

The diastases from *Aspergillus oryzæ* and *Penicillium glaucum*, and the hydrogenases which are identical with catalase (Loew, Abstr., 1901, i, 435), all energetically decompose hydrogen peroxide, but do not yield the blue coloration with guaiaconic acid; this anomaly is due to the reducing action of the hydrogenases. The presence of these enzymes would therefore suffice to mask that of any oxydases in a mixture of diastasic ferments. G. T. M.

Differences between Diastases. By Horace M. Vernon (*J. Physiol.*, 1902, **28**, 156—174).—The progress of the colour reactions with dilute iodine during the progress of starch digestion varies considerably according to the nature of the diastase employed. The different diastases of animal and vegetable origin are therefore considered to be different substances. W. D. H.

Catalytic Properties of the Hydrogenases; Identification of Loew's "Catalase" with De Rey-Pailhade's "Philothion." By M. Emm. Pozzi-Escot (*Bull. Soc. Chim.*, 1902, [iii], **27**, 280—288).—Philothion (compare Abstr., 1888, 1101) does not give a blue coloration with tincture of guaiacum and hydrogen peroxide, the usual reaction of the diastases. It decomposes hydrogen peroxide, however, the amount of oxygen liberated being proportional to the amount of philothion employed, and the velocity of decomposition being a function only of the "active mass." The amount of oxygen evolved is at first comparatively large, but gradually diminishes, and at last the evolution of gas ceases; the maximum action takes place at a temperature between 30° and 40°. The action does not appear to be purely catalytic, but rather chemical, and at length ceases owing to the oxidation of the hydrogenase. The action of "paralysing" or retarding substances on the reaction was also studied, and it was found that mercuric chloride and silver nitrate are exceedingly powerful retarders, and generally that salts with an acid reaction have the most powerful retarding effect, whilst alkalis have an accelerating action.

On account of the agreement between philothion and catalase (compare Abstr., 1901, i, 435) with regard to the decomposition of hydrogen peroxide, the action of salts on that decomposition, and other properties, such as the production of hydrogen sulphide from sulphur, the author concludes that philothion and catalase are identical. He is not able to confirm Loew's statement as to the oxidation of quinol by means of catalase. A. F.

Phenolphthalin as a Reagent for the Oxidising Ferments. By J. H. Kastle and O. M. Shedd (*Amer. Chem. J.*, 1901, **26**, 526—539).—The oxidation of phenolphthalin to phenolphthalein by the oxidising ferment of potato extract has been investigated. The reaction was carried out in acid solution and the depth of colour developed on adding alkali served as a guide to the extent of oxidation which had taken place. An aqueous solution of the oxydase of potato loses its oxidising property on standing. The oxydase is distributed throughout the whole of the potato, the hypodermal layer being possibly richest in it. The oxidation is apparently effected by the oxydase itself, and this does not seem to act simply as an oxygen-carrier. The action of the oxydase proceeds slowly, and phenolphthalin is an excellent reagent for following its course; the reaction reaches its maximum at about the end of an hour.

The particular oxydase which turns guaiacum resin blue directly and oxidises phenolphthalin, is not confined to the potato, but is widely distributed in the vegetable kingdom and occurs also in human saliva. The oxydase is probably not identical with the catalase described by Loew (U.S. Dept. Agric., Report No. 68). J. McC.

Nature of certain of the Oxidising Ferments. By J. H. Kastle and A. S. Loevenhart (*Amer. Chem. J.*, 1901, **26**, 539—566). —Guaiacum becomes blue immediately when added to a potato the skin of which has been removed, but the blue colour only appears on standing when the guaiacum is applied to the interior pulp of the potato. The oxidising substance of the potato is unstable, but its stability can be increased by certain antiseptics (chloroform or thymol). Schönbein's observation that atmospheric oxygen is essential for the formation of guaiacum-blue by the oxygen-carrier of the potato has been definitely confirmed. Organic peroxides (for example, benzoyl peroxide) give an immediate blue coloration with guaiacum. The oxidising substance of the potato is very easily soluble in water, but is insoluble in ethyl or amyl alcohol. Various substances (particularly hydrocyanic acid, salicylic acid, hydroxylamine, phenylhydrazine, and sodium thiosulphate) inhibit the turning blue of guaiacum by potato extract; silver nitrate and mercuric chloride seem to be without influence. The same substances which inhibit the reaction of the potato extract exert a similar influence on the turning blue of guaiacum by peroxides (both organic and inorganic), and this, coupled with the inactivity of silver and mercuric salts, leads the authors to conclude that the oxidising substance of the potato is not a true soluble ferment but an organic peroxide. They explain its action by Baeyer and Villiger's theory (Abstr., 1900, i, 437); it acts as a carrier of oxygen in the same way that benzaldehyde does, but is not a true catalytic agent. Nothing definite can be said of the nature of the substance, but it may possibly be an aldehyde. J. McC.

Aromatic Arsenic Compounds. By AUGUST MICHAELIS (*Annalen*, 1902, **321**, 141—248. Compare this vol., i, 411).—[With W. WEBER.]—Diphenylchloroarsine, $AsPh_2Cl$ (b. p. 333°), prepared either by heating phenylchloroarsine and mercury diphenyl or by distilling triphenylarsinedichloride, yields diphenylarsinic acid, $AsPh_2O\cdot OH$, when oxidised by chlorine water. The acid, which can also behave as a base, yields the *nitrate*, $AsPh_2O\cdot ONO_3$, on treatment with a cold mixture of concentrated nitric and sulphuric acids; this derivative separates from glacial acetic acid in white needles and melts at 125°; it is insoluble in the other organic solvents.

Dinitrodiphenylarsinic acid, $As(C_6H_4\cdot NO_2)_2O\cdot OH$, resulting from the action of the heated mixed acids, crystallises from glacial acetic acid in yellow prisms and melts at 256°; it is very sparingly soluble in water, alcohol, benzene, chloroform, or ether. The salts of the alkalis and alkaline earth metals are easily soluble, the *barium* salt crystallises in pale yellow flakes, the normal *silver* salt is a white precipitate, the *copper* salt has the composition $(C_6H_4\cdot NO_2)_2AsO\cdot OCu\cdot OH$.

The preceding nitro-acid does not yield amino-derivatives on reduction, but *tetrabromodiaminodiphenylarsinic acid*,

$$As(C_6H_2Br_2\cdot NH_2)_2O_2H,$$

melting indefinitely at 187°, is obtained by heating diaminodiphenyl sulphide with bromine water on the water-bath; at higher temperatures the *hexabromodiaminodiphenylarsinic acid* is produced; this substance is a very stable, white powder melting at 287°.

Tetranitrotetraphenyldiarsine, $As(C_6H_4\cdot NO_2)_2\cdot As(C_6H_4\cdot NO_2)_2$, prepared by heating a glacial acetic acid solution of dinitrodiphenylarsinic acid with phosphorous acid, separates on cooling in lustrous leaflets and melts at 200°; the *tetra-amino*-compound resulting from the prolonged action of the reducing agent is amorphous; its *tetra-acetyl* derivative, a white pulverulent substance, melts at 162°. Tetraphenyldiarsine is similarly produced from diphenylarsenious oxide.

Dinitrodiphenylchloroarsine, $As(C_6H_4\cdot NO_2)_2Cl$, is produced by passing chlorine into a benzene solution of tetranitrotetraphenyldiarsine; a *trichloride* is simultaneously formed which changes into the monochloride on adding to the solution an excess of the tetranitro-compound. The monochloride crystallises in pale yellow needles and melts at 112°; it dissolves in alkaline solutions, yielding salts of dinitrodiphenylarsenious acid.

Dinitrodiphenylbromoarsine, $As(C_6H_4\cdot NO_2)_2Br$, forms transparent, colourless leaflets melting at 93°. The *tribromoarsine*, $(C_6H_4\cdot NO_2)_2AsBr_3$, is a solid substance readily decomposed by moisture, yielding dinitrodiphenylarsinic acid.

Diphenylarsenious acid is not stable, but its *phenyl ester*, $AsPh_2\cdot OPh$, is a colourless liquid boiling at 230—231° under 15 mm. pressure, and having a sp. gr. 1·3113 at 11°; it solidifies in a freezing mixture and is hydrolysed by water at 100° into phenol and diphenylarsenious oxide. This ester differs very materially from its isomeride, triphenylarsine oxide, $AsPh_3O$, the isomerism resembling that which obtains with the corresponding phosphorous compound.

Phenoxydiphenylarsine chloride, $AsPh_2Cl_2\cdot OPh$, obtained by passing chlorine into a petroleum solution of the phenyl ester, crystallises in needles, melts at 121—122°, and is hydrolysed by water into diphenylarsinic acid, phenol, and hydrogen chloride. The corresponding *bromide*, $AsPh_2Br_2\cdot OPh$, forms yellowish-red crystals melting at 100°.

Dinitrodiphenylarsenious acid, $As(C_6H_4\cdot NO_2)_2\cdot OH$, resulting from the action of water or alkaline solutions on dinitrodiphenylchloroarsine or the corresponding bromo-compound, crystallises from alcohol in white, felted needles, melts at 149°, and reduces silver nitrate ; its salts are very unstable.

Diphenylarsenious sulphide, $S(AsPh_2)_2$, obtained by passing hydrogen sulphide in an alcoholic solution of diphenylarsenious oxide, crystallises from alcohol in white, silky needles melting at 67° ; it is soluble in the ordinary organic solvents but not in aqueous solutions of the alkali hydroxides or monosulphides. Concentrated hydrochloric acid decomposes the sulphide, regenerating diphenylchloroarsine, the reverse change occurs slowly in warm alcoholic solution.

Dinitrodiphenylarsenious sulphide, $S[As(C_6H_4\cdot NO_2)_2]_2$, separates, on adding alcohol to hot benzene solution of sulphur and tetranitrotetraphenyldiarsine, in aggregates of yellow needles melting at 156°. The *diamino*-derivative, $S[As(C_6H_4\cdot NH_2)_2]_2$, results from the action of a concentrated ammoniacal ammonium sulphide solution on the preceding compound and is isolated in the form of its hydrochloride on adding hydrochloric acid. The base is a white, amorphous powder and melts at 110° ; the *sulphate*, $S[As(C_6H_4\cdot NH_2)_2]_2,2H_2SO_4$, separates from aqueous solutions in snow white needles ; the *acetyl* derivative separates in floccula melting at 175°.

Tetraphenylarsenic disulphide, $S_2(AsPh_2)_2$, prepared by the action of ammoniacal ammonium sulphide solution on diphenylarsinic acid, is precipitated on adding hydrochloric acid, and crystallises from alcohol in white leaflets sintering at 60° and melting at 110°. *Tetranitrotetraphenylarsenic trisulphide*, $As_2S_3(C_6H_4\cdot NO_2)_4$, produced by boiling tetranitrotetraphenyldiarsine with sulphur suspended in benzene, is a yellow, crystalline substance melting at 69°.

[With H. PREDARI.]—*Phenyl*-p-*tolylchloroarsine*, $C_7H_7\cdot AsPhCl$, prepared by boiling a mixture of phenylchloroarsine and mercurydi-*p*-tolyl, is a colourless, oily liquid, boiling at 215—237° under 29 mm. and at 215—240° under 50 mm. pressure ; with chlorine, it yields a white, crystalline trichloride and with alcoholic potassium hydroxide a yellow, syrupy oxide, $(C_7H_7\cdot AsPh)_2O$, the latter substance taking up chlorine to form an oxychloride, $(AsPh\cdot C_7H_7)_2OCl_4$ crystalling in white needles.

Phenyl-p-*tolylarsenious sulphide*, $(C_7H_7\cdot AsPh)_2S$, is an oil. *Phenyl*-p-*tolylarsinic acid*, $C_7H_7\cdot AsPh\cdot O_2H$, crystallises from water in felted, white needles and melts at 158—160°.

Phenyl-p-*tolylethylarsine*, $C_7H_7\cdot AsEtPh$, formed by the action of zinc ethyl, is a colourless oil having an unpleasant odour and boiling at 210—225° under 50 mm. pressure ; the *dichloride*, formed by direct addition of chlorine, crystallises in white needles melting at 148°.

Phenyl-p-*tolylmethylethylarsonium iodide*, $C_7H_7\cdot AsMeEtPhI$, produced from methyl iodide and the preceding tertiary arsine, crystallises in white needles which, when deposited from water or alcohol, melt at 150—151° or at 145° respectively ; the alcoholic solution of this asymmetric iodide has a slight optical rotation, but the salt could not be resolved into its active components either by tartaric or aspartic acid, or by the action of fungi; the *chloride* is not crystalline but the *platinichloride* separates in yellowish-red, triclinic needles and melts at 214°.

Phenyl-p-*tolyldiethylarsonium iodide*, $C_7H_7\cdot AsPhEt_2I$, crystallises from water in monoclinic needles and melts at 148°. The tertiary arsine forms crystalline, quaternary iodides with benzyl and *n*- and *iso*-propyl iodides; the benzyl chloride does not crystallise.

[With LUDWIG.]—Triphenylarsine, which is conveniently prepared by the action of sodium on an ethereal solution of arsenious chloride and bromobenzene, yields a *platinichloride*, $AsPh_3,H_2PtCl_6$, crystallising in pale yellow leaflets and melting at 285°. *Triphenylarsine dichloride*, $AsPh_3Cl_2$, produced by passing chlorine into triphenylarsine dissolved in dry carbon tetrachloride, sinters at 158° and melts at 204—205°; in the presence of moisture, it readily passes into the more stable *hydroxychloride*, $AsPh_3Cl\cdot OH$, a substance melting at 171°, which is more directly obtained by passing chlorine into the tertiary base dissolved in commercial chloroform. The hydroxychloride yields a *platinichloride* of exceptional composition, $(AsPh_3Cl\cdot OH)_3,PtCl_4$, which crystallises in yellow needles and melts at 180—182°.

Triphenylarsine dibromide, $AsPh_3Br_2$, separates in white crystals, sinters at 165°, and melts at 215°.

Triphenylarsine tetraiodide, $AsPh_3I_4$, formed by mixing its generators in anhydrous solvents, separates from ether in steel-blue needles and melts at 142—144°; the analogous compound, $AsPh_3Br_2I_2$, obtained from a mixture of bromine and iodine, crystallises in yellowish-red needles and melts at 120—121°.

Triphenylarsine hydroxide (m. p. 115—116°), $AsPh_3(OH)_2$, readily obtained from the corresponding chloride or oxychloride by the action of ammonia, is a basic substance yielding the *normal nitrate*, $AsPh_3(NO_3)_2$, melting at 99—100°, the basic nitrate, $OH\cdot AsPh_3\cdot NO_3$, melting at 160—161°, and the *basic chromate*, $AsPh_3(OH)\cdot HCrO_4$, which is a yellow-red precipitate.

[With K. ULRICH.]—Triphenylmethylarsonium iodide combines with chlorine to form a *dichloride*, $AsPh_3MeICl_2$, which crystallises from alcohol, acetone, or glacial acetic acid in yellow leaflets and melts at 144°; this additive product is also produced either by the action of hypochlorous acid or the iodide, or by treating the quaternary chloride with iodinechloride. *Triphenylmethylarsonium hydroxide*, $AsPh_3Me\cdot OH$, obtained by shaking the iodide with moist silver oxide, crystallises in prisms and melts at 125—126°; it has an alkaline reaction, and when heated at 100° decomposes into methyl alcohol and triphenylarsine; the solution rapidly absorbs carbon dioxide, forming the soluble *carbonate*, which separates in large, transparent plates.

[With E. WEISS.]—*Triphenylmethylarsonium chloride*, produced either by neutralising the hydroxide with hydrochloric acid, or by digesting the iodide with silver chloride, crystallises in white needles and melts at 121°; the *platinichloride*, $(AsPh_3Me)_2PtCl_6$, crystallises in yellowish-red needles melting at 224—225°; the *nitrate*,

$$AsPh_3Me\cdot NO_3,$$

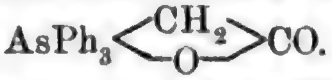
separates in long needles and on treatment with a mixture of concentrated nitric and sulphuric acids, yields a small amount of *trinitrotriphenylarsonium nitrate*, separating from alcohol as a yellow powder melting at 195°; it is accompanied by a red product, probably an isomeride.

Triphenylethylarsonium iodide, $AsPh_3EtI$, obtained in small yield from its generators at the temperature of the water-bath, crystallises in lustrous needles melting at 158°; the *platinichloride* melts at 221°.

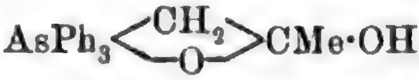
Triphenyliodomethylarsonium iodide, $CH_2I{\cdot}AsPh_3I$, produced from methylene iodide and triphenylarsine at 130°, crystallises from dilute alcohol in white, silky needles melting at 227°, and yields *triphenylchloromethylarsonium iododichloride*, $CH_2Cl{\cdot}AsPh_3{\cdot}ICl_2$, separating in yellow crystals melting at 138°, and giving rise to triphenylarsonium hydroxide on treatment with sodium hydroxide.

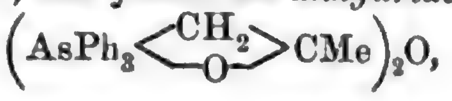
Triphenyliodomethylarsonium chloride, $CH_2I{\cdot}AsPh_3Cl$, crystallises in needles and melts at 208°; *hydroxymethyltriphenylarsonium chloride*, $OH{\cdot}CH_2{\cdot}AsPh_3Cl$, obtained by treating the salt, $CH_2I{\cdot}AsPh_3I$, successively with silver oxide and hydrochloric acid, melts at 112°; the *platinichloride*, $(OH{\cdot}CH_2{\cdot}AsPh_3)_2PtCl_6$, melts at 224°; the *iodide* forms yellow, flattened needles and melts at 171°

Hydroxyethyltriphenylarsonium chloride, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}AsPh_3Cl$, prepared by heating triphenylarsine with ethylene chlorohydrin, crystallises in colourless needles, melts at 215°, and gives a *platinichloride* melting at 223°.

Triphenylarsenobetaine hydrochloride, $CO_2H{\cdot}CH_2{\cdot}AsPh_3Cl$, produced from triphenylarsine and chloroacetic acid, forms white, soluble needles melting at 145°; the *platinichloride* melts at 194°. *Triphenylarsenobetaine*, $CO_2H{\cdot}CH_2{\cdot}AsPh_3{\cdot}OH$, set free from the hydrochloride by alcoholic potassium hydroxide, crystallises in soluble, white needles, melts at 125°, and yields the *anhydride*,  $AsPh_3\left\langle\begin{matrix}CH_2\\ O\end{matrix}\right\rangle CO$.

Triphenylmethylarsenoketobetaine hydrochloride, $COMe{\cdot}CH_2{\cdot}AsPh_3Cl$, prepared by heating triphenylarsine with chloroacetone, separates in quadratic crystals and melts at 172°; the *platinichloride* is a reddish-brown precipitate.

Triphenylmethylarsenoketobetaine,  $AsPh_3\left\langle\begin{matrix}CH_2\\ O\end{matrix}\right\rangle CMe{\cdot}OH$, produced by treating the preceding salt with alkalis, crystallises in nacreous leaflets, melts at 123°, and yields the *anhydride*,



$$\left(AsPh_3\left\langle\begin{matrix}CH_2\\ O\end{matrix}\right\rangle CMe\right)_2O,$$

melting at 194°.

Triphenylmethylarsenoketobetaine hydrobromide and hydriodide are soluble in water or alcohol and melt at 165° and 161° respectively.

Triphenylphenacylarsonium bromide, $AsPh_3Br{\cdot}CH_2{\cdot}COPh$, obtained from triphenylarsine and bromoacetophenone, crystallises in silky, felted needles and melts at 178°; the *chloride* and *iodide* melt at 166° and 157° respectively; these salts are soluble in water or alcohol. The *platinichloride* melts at 191°; the *nitrate*, which is insoluble in cold water, dissolves in alcohol, crystallises in needles, and melts at 184°.

Trinitrotriphenylarsine, $As(C_6H_4{\cdot}NO_2)_3$, prepared by the action of phosphorous acid on the trinitrotriphenylarsine oxide obtained by nitrating triphenylarsine, is a yellow, crystalline powder melting at 250°.

Trinitrotriphenylarsine dibromide, $As(C_6H_4{\cdot}NO_2)_3Br_2$, and *dichloride* melt at 204° and 228° respectively.

Trichlorotrinitrotriphenylarsine oxide, $As(C_6H_3Cl{\cdot}NO_2)_3O$, produced from the preceding chloride by the action of potassium hydroxide, is a white, crystalline mass melting at 257°, yielding the *dibromide*, $As(C_6H_3Cl{\cdot}NO_2)_3Br_2$, melting at 209°, and the arsine, $As(C_6H_3Cl{\cdot}NO_2)_3$, on treatment with phosphorous acid; this base is soluble in the ordinary organic solvents and melts at 252°.

Trinitrotriphenylarsine oxide, on reduction, yields the corresponding triamine, the sulphate of which is stable in air, whilst its *tribenzoyl* derivative is a crystalline powder melting at 271°. Triaminotriphenylarsine cannot be diazotised, but it yields a bromo-derivative,

$$As(C_6HBr_3{\cdot}NH_2)_3(OH)_2,$$

with excess of bromine water. The *amino*-compound,

$$As(C_6H_4{\cdot}NO_2)_2{\cdot}C_6H_4{\cdot}NH_2,$$

produced by reducing the trinitro-compound with hydrogen sulphide in glacial acetic acid solution, has no basic properties and melts at 205°.

Barium triphenylarsineoxidesulphonate, $Ba_3[AsO(C_6H_4{\cdot}SO_3)_3]_2$, obtained by sulphonating triphenylarsine with concentrated sulphuric acid at 100° and treating the product with barium carbonate, is a pale red, soluble, crystalline powder; the free acid was not isolated.

[With F. LAUTERWALD.]—Diphenyl-*p*-tolylarsine, $AsPh_2{\cdot}C_7H_7$, prepared from the interaction of *p*-tolylchloroarsine, bromobenzene, and sodium, is obtained crystalline with considerable difficulty; it melts at 50°; the *mercurichloride*, $AsPh_2{\cdot}C_7H_7,HgCl_2$, melts at 147°, and the *platinichloride*, $(AsPh_2{\cdot}C_7H_7)_2,H_2PtCl_6$, at 233°.

*Diphenyl-*p*-tolylarsine hydroxide*, $C_7H_7{\cdot}AsPh_2(OH)_2$, obtained by adding bromine to the arsine and treating the product with hot potassium hydroxide solution, melts at 68°; the *basic nitrate*, $C_7H_7{\cdot}AsPh_2(OH){\cdot}NO_3$, crystallises in yellow needles and melts at 125°; the *sulphide*, $C_7H_7{\cdot}AsPhS$, resulting from the action of hydrogen sulphide on an alcoholic solution of the hydroxide, forms a crystalline, granular mass and melts at 135°.

*Diphenyl-*p*-tolylmethylarsonium iodide*, $C_7H_7{\cdot}AsPh_2MeI$, formed by the direct union of its generators, separates in druses of white needles and melts at 152°; the *chloride* is oily, the *platinichloride* melts at 209°.

*Diphenyl-*p*-tolylethylarsonium iodide*, $C_7H_7{\cdot}AsPh_2EtI$, is an oil, but the corresponding *platinichloride* separates in red crystals and melts at 220°.

Diphenyloxyarsinobenzoic acid, $AsPh_2O{\cdot}C_6H_4{\cdot}CO_2H$, obtained by the oxidation of *p*-tolyldiphenylarsine with permanganate, melts at 253—254°; its *silver* and *barium* salts are both soluble.

Ethyl diphenyldichloroarsinobenzoate, $AsPh_2Cl_2{\cdot}C_6H_4{\cdot}CO_2Et$, produced by saturating an alcoholic solution of the preceding acid with hydrogen chloride, separates on cooling in white crystals melting at 133°.

Diphenylsulphoarsinobenzoic acid, $AsPh_2S{\cdot}C_6H_4{\cdot}CO_2H$, resulting from the action of hydrogen sulphide on the oxy-acid, melts at 178°.

*Phenyldi-*p*-tolylarsine*, $AsPh(C_7H_7)_2$, prepared from phenylchloroarsine, bromotoluene, and sodium, crystallises from alcohol in white rhombohedra and melts at 101°; the *mercurichloride*, $AsPh(C_7H_7)_2,HgCl_2$, *platinichloride*, and *dichloride*, $AsPh(C_7H_7)_2Cl$, melts at 210°, 256°, and 194° respectively. The dichloride, in contact with moisture, gives rise to an *oxychloride*, $AsPh(C_7H_7)_2OH\cdot Cl$, which melts at 142—143°; the *oxybromide* is obtained in a similar manner.

Phenyldi-p-*tolylarsine oxide*, obtained by the action of alkalis on the preceding haloid derivatives, is a white powder melting at 81°; it yields a *basic nitrate* crystallising in rosettes of needles and melting at 94°, and also a *sulphide*, $AsPh(C_7H_7)_2S$, melting at 144°.

Phenyldi-p-*tolylmethylarsonium iodide*, $AsPh(C_7H_7)_2MeI$, crystallises from water in long, white needles, which become yellow on exposure to light and melt at 84°; the *platinichloride* crystallises in yellow needles and melts at 222°; the corresponding *ethiodide*, $(C_7H_7)_2AsPhEtI$, melts at 125°.

Phenyloxyarsinodibenzoic acid, $AsPhO(C_6H_4\cdot CO_2H)_2$, prepared by oxidising phenyldi-*p*-tolylarsine with alkaline permanganate solution, is a white, crystalline powder not melting below 300°; its silver and copper salts are insoluble white and blue powders respectively, the latter containing $1H_2O$; the *barium* salt is readily soluble. *Diethyl phenyldichloroarsinodibenzoate*, $AsPhCl_2(C_6H_4\cdot CO_2Et)_2$, obtained by saturating an alcoholic solution of the acid with hydrogen chloride, crystallises in aggregates of needles and melts at 176°.

Phenyl-p-*tolyloxyarsinobenzoic acid*, also produced by the oxidation of di-*p*-tolylphenylarsine, does not melt below 300°; its silver salt, $C_7H_7\cdot AsPhO\cdot C_6H_4\cdot CO_2Ag$, crystallises in slender needles; the *dichloroester*, $C_7H_7\cdot AsPhCl_2\cdot C_6H_4\cdot CO_2Et$, is very hygroscopic and melts at 94°.

Tri-p-*tolylarsine*, prepared by the general method, separates in triclinic crystals and melts at 146°; the *mercurichloride*, a white, crystalline powder, melts at 246°. The *dichloride*, $As(C_7H_7)_3Cl_2$, and the *oxychloride* are crystalline substances, melting respectively at 228—230° and 185°; the *dibromide* melts at 245°, and the di-iodide at 172°. A *tetraiodide*, $C_7H_7AsI_4$, resulting from the action of excess of iodine, forms steel-grey needles melting at 153°. The *hydroxide*, $As(C_7H_7)_3(OH)_2$, crystallises from alcohol in needles and melts at 96°; the *sulphide*, $As(C_7H_7)_3S$, separates in lustrous leaflets melting at 170—171°.

Tri-p-*tolylmethylarsonium iodide*, $As(C_7H_7)_3MeI$, melts at 179°, the *chloride* at 87°, the *dichloroiodide*, $As(C_7H_7)_3MeICl_2$, at 146°; the *platinichloride* crystallises from dilute alcohol in reddish-brown, highly refractive prisms.

Tri-p-*tolyliodomethylarsonium iodide*, $CH_2I\cdot As(C_7H_7)_3I$, resulting from the direct action of methylene iodide on tri-*p*-tolylarsine, separates from alcohol in well-defined crystals melting at 215°.

Tri-p-*tolylethylarsonium iodide*, $As(C_7H_7)_3EtI$, crystallises in colourless needles and melts at 158°. *Tri*-p-*tolylallylarsonium bromide*, $As(C_7H_7)_3\cdot C_3H_5I$, prepared by heating allyl bromide with the tertiary arsine at 100°, crystallises from water in white prisms and melts at

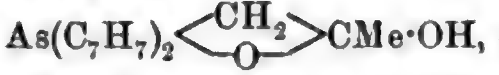
82°; this substance takes up bromine, forming *tri*-p-*tolyldibromopropylarsonium bromide*, $As(C_7H_7)_3C_3H_5BrI$, which melts at 112°.

Tri-p-*tolylallylarsonium iodide* separates in colourless prisms and melts at 141°; the corresponding *chloride* is a yellow oil, yielding a *platinichloride* which separates as a red powder and melts at 225°.

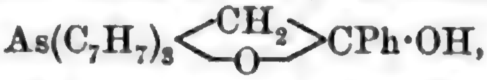
Tri-p-*tolylarsenobetaine hydrochloride*, $As(C_7H_7)_3Cl{\cdot}CH_2{\cdot}CO_2H$, obtained as a white, crystalline mass melting at 146°, furnishes a *platinichloride* melting at 206°; the free betaine is not readily purified.

[With W. KRAHE.]—*Acetonyltri*-p-*tolylarsonium chloride*,

$$As(C_7H_7)_3Cl{\cdot}CH_2Ac,$$

decomposes at 170°; the free *betaine*,  $As(C_7H_7)_2<\genfrac{}{}{0pt}{}{CH_2}{O}>CMe{\cdot}OH$, crystallises from dilute alcohol in lustrous needles and melts at 113°; the *platinichloride*, $[As(C_7H_7)_3{\cdot}CH_2Ac]_2PtCl_6$, forms yellow leaflets melting at 210°; the *bromide*, $As(C_7H_7)_3Br{\cdot}CH_2Ac$, melts at 159° and the *iodide* at 144°.

Tri-p-*tolylphenacylarsonium chloride*, $As(C_7H_7)_3Cl{\cdot}CH_2{\cdot}COPh$, crystallises in white needles melting at 159°; the *platinichloride* forms yellowish-red needles and melts at 205°, the betaine,



$$As(C_7H_7)_3<\genfrac{}{}{0pt}{}{CH_2}{O}>CPh{\cdot}OH,$$

separates from alcohol in aggregates of needles and melts at 160°; the *bromide* and *iodide* melt at 182° and 148° respectively.

Trinitrotri-p-*tolylarsine*, $As(C_7H_6{\cdot}NO_2)_3$, produced by the action of phosphorous acid on trinitrotri-*p*-tolylarsine oxide (m. p. 212°), the product of the nitration of the tertiary tolylarsine, crystallises in white needles and melts at 201°.

Trichlorotrinitrotri-p-*tolylarsine chloride*, $As(C_6H_3Cl{\cdot}NO_2)_3Cl_2$, which results from the action of dry chlorine on the nitroarsine dissolved in chloroform, melts at 170° and yields *triaminotri*-p-*tolylarsine*,

$$As(C_7H_6{\cdot}NH_2)_3,$$

on reduction with tin and hydrochloric acid; this base is obtained in white prisms melting at 198°, its *hydrochloride*, $As(C_7H_6{\cdot}NH_2)_3,3HCl$, crystallising in white needles. The *sulphate* is insoluble and the *triacetyl* derivative melts at 228°.

Triaminotri-p-*tolylarsine sulphide*, $As(C_7H_6{\cdot}NH_2)_3S$, produced from the triamine and alcoholic ammonium sulphide, is separated from sulphur by alcohol and carbon disulphide; it is insoluble in the organic solvents but dissolves in the dilute mineral acids, sulphuric acid giving rise to the *acid sulphate*, $2As(C_7H_6{\cdot}NH_2)_3S,3H_2SO_4$, which is soluble in hydrochloric acid. The *methiodide*, $As(C_7H_6{\cdot}NMe_2)_3MeI$, obtained by heating the triaminoarsine with excess of methyl iodide, is a white powder melting indefinitely at 135°.

Tribenzyltriaminotri-p-*tolylarsine*, $As(C_7H_6{\cdot}NH{\cdot}CH_2Ph)_3$, is obtained the form of its hydrochloride by the action of benzyl chloride.

[With HERRMANN EISENLOHR.]—*Tri*-m-*tolylarsine*, prepared from *m*-bromotoluene by the general method, crystallises from alcohol or ether in rhombic, tabular crystals [$a:b:c = 1{\cdot}00872:1:1{\cdot}0355$], melts at 96° and has a sp. gr. 1·31 at 18°; the *mercurichloride* melts at 174°, the *hydroxychloride* and *hydroxybromide*, obtained in well-defined crystals, melt at 205° and 190° respectively; the *oxide*, a white, crystalline mass, melts at 170°; the *sulphide*, which forms silvery needles, melts at 186°.

Tri-m-*tolylmethylarsonium iodide*, $As(C_7H_7)_3MeI$, crystallises from water in rhombic prisms and melts at 181°; the *chloride* is oily, the *platinichloride* is a light yellow precipitate, the *ethiodide* separates in modified, triclinic rhombohedra and melts at 130°. *Tri*-m-*tolyl*-n-*propylarsonium iodide*, $As(C_7H_7)_3Pr^{\alpha}I$, slowly formed by the direct combination of the tertiary arsine and propyl iodide at the ordinary temperature, separates in needles and melts at 143°; the iso*propyl* quaternary iodide melts at 162°. The interaction of the tertiary arsine and benzyl chloride at 30—40° gives rise to *tri*-m-*tolylbenzylarsonium chloride*, which melts at 102°.

[With M. Heine.]—*Tri*-1 : 3-*xylyl*-4-*arsine*, $As(C_8H_9)_3$, prepared by the general method from 4-bromo-*m*-xylene, crystallises from light petroleum in lustrous, transparent prisms melting at 166°; the *mercurichloride* melts at 257°, the *sulphide*, which crystallises in silky prisms, melts at 145°. The oxide, $As(C_8H_9)_3O$, formed as a tarry mass by the dehydration of the *hydroxide*, $As(C_8H_9)_3(OH)_2$, a substance resulting from the action of alkaline solutions on the dibromide of the tertiary arsine.

Tri-1 : 3-*xylylmethyl*-4-*arsonium iodide*, $As(C_8H_9)_3MeI$, melts at 179°; the *chloride* is not crystallisable, but yields a platinichloride separating in reddish-brown crystals melting at 245°; the ethiodide could not be obtained.

[With A. Schaeuble.]—*Tri*-p-*xylylarsine*, prepared from bromo-*p*-xylene and obtained in white prisms melting at 157°, yields a *mercurichloride* melting at 236°, and a crystalline *chloride*, $(C_8H_9)_3AsCl_2$; its *oxide* is not crystallisable. The *methiodide*, crystallising in plates, melts at 175°; the platinichloride, obtained in yellow needles, melts at 250°.

[With Ad. Rotter.]—*Phenyldi*-1 : 3-*xylylarsine*, $As(C_8H_9)_2Ph$, prepared by the interaction of 4-bromo-*m*-xylenephenylchloroarsine and sodium, crystallises in tabular, triclinic prisms and melts at 99°; the *platinichloride*, separating in yellow, felted needles, decomposes near 300°; the *mercurichloride*, which is obtained in white needles, melts at 224°; the *dichloride* and *oxychloride* melt at 176° and 186° respectively, whilst the *periodide*, $As(C_8H_9)_2PhI_4$, which forms reddish-violet crystals, melts at 127°. The *hydroxide* and *oxide*, which melt respectively at 112° and 120°, give rise to the *basic nitrate*,

$$OH\cdot AsPh(C_8H_9)_2\cdot NO_3,$$

a compound forming transparent crystals and melting at 126°. The tertiary arsine forms a sulphide and ethiodide with great difficulty, the latter compound melting at 157°. *Phenyldi*-1 : 3-*xylylmethylarsonium iodide*, readily produced from the arsine and methyl iodide, melts at 184° and yields the quaternary *hydroxide* melting at 122°.

Trinitrophenyldi-1 : 3-*xylylarsine oxide*, $AsO(C_8H_8\cdot NO_2)_2\cdot C_6H_4\cdot NO_2$, obtained by treating the arsine with concentrated nitric and sulphuric acids, separates from alcohol in pale yellow crystals melting at 245°.

Phenyloxyarsinoditolyldicarboxylic acid, $AsPhO(C_6H_3Me\cdot CO_2H)_2$, and *phenyloxyarsinodiphenyltetracarboxylic acid*, $AsPhO[C_6H_3(CO_2H)_2]_2$, produced by heating the arsine with nitric acid of sp. gr. 1·2 at 110—170°, melt respectively at 196° and 213°.

[With SCHNEEMANN.]—*Tri-p-ethylphenylarsine*, $As(C_6H_4Et)_3$, prepared from *p*-bromoethylbenzene by the general method, melts at 78° and yields a *mercurichloride*, *dichloride*, *dibromide*, *hydroxide*, and *sulphide* melting respectively at 132°, 246°, 212°, 180°, and 123°. The *methiodide* and the *trinitro*-derivative, $AsO(C_6H_3Et\cdot NO_2)_3$, of the corresponding oxide are crystalline and melt at 126° and 232°.

[With D. VON KARCHOWSKI.]—*Tri-ψ-cumylarsine*, prepared in the ordinary way, crystallises in snow-white needles and melts at 223°; its *dibromide* and *hydroxybromide* melt respectively at 224—225° and 108° and give rise to the *hydroxide*, $As(C_9H_{11})_3(OH)_2$, which crystallises from dilute alcohol in needles containing $4H_2O$; these, on desiccation, over concentrated sulphuric acid yield the pulverulent *oxide* melting at 227—228°.

[With AD. ROTTER.]—*Phenyl*-di-*ψ-cumylarsine*, prepared from phenylchloroarsine, bromo-ψ-cumene, and sodium, melts at 138·5° and yields the *platinichloride* crystallising in yellow aggregates and melting at 287°; the *aurichloride* forms colourless druses and melts at 177°; the *mercurichloride*, $AsPh(C_9H_{11})_2,HgCl_2$, crystallises in needles and melts at 233°; the *dichloride*, $AsPh(C_9H_{11})_2Cl_2$, is a crystalline powder melting at 217°. The *hydroxychloride*, *dibromide*, *di-iodide*, and *hydroxyiodide* melt respectively at 173—175°, 177°, 163·5°, and 153°, and give rise to the *hydroxide*, $AsPh(C_9H_{11})_2(OH)_2$, which separates in colourless prisms melting at 113—114°, and yields, on heating or desiccation, the *oxide* melting at 162·5°. The *sulphide*, obtained by heating the tertiary arsine with alcoholic ammonium polysulphide at 110°, melts at 135°. The *methylarsonium iodide*, the *chloride*, and *platinichloride* melt respectively at 179°, 192°, and 266·5°. The quaternary *hydroxide* crystallises in needles softening at 147° and melting at 151°. The *ethylarsonium iodide* melts at 189°.

Trinitrophenyldi-ψ-cumylarsine oxide, $AsO(C_9H_{11}\cdot NO_2)_2\cdot C_6H_4\cdot NO_2$, produced by nitrating the tertiary arsine, melts at 163°.

Phenyloxyarsinodixylyldicarboxylic acid, $AsOPh(C_6H_2Me_2\cdot CO_2H)_2$, *phenyloxyarsinoditolyltetracarboxylic acid*, $AsOPh[C_6H_2Me(CO_2H)_2]_2$, and *phenyloxyarsinodiphenylhexacarboxylic acid*, $AsOPh[C_6H_2(CO_2H)_3]_2$, result from the action of nitric acid of sp. gr. 1·2 on the tertiary arsine at 110—180°; the first two melt at 199° and 213° respectively, whilst the third yields an anhydride melting at 275°. The *silver* salt of the anhydrotetracarboxylic acid is a white powder; the corresponding *tetraethyl* ester crystallises in silky needles and melts at 193°.

[With W. OBERG.]—*Tri-p-cumylarsine*, $As(C_6H_4Pr)_3$, obtained from *p*-bromocumene by the general method, crystallises in colourless prisms melting at 139—140°; the *mercurichloride*, $As(C_9H_{11})_3HgCl_2$, separates in white needles and melts at 243°; the *dichloride* forms white needles, melts at 276°, and yields a *platinichloride*, $[As(C_9H_{11})_3]_2PtCl_6$, crystallising in golden-yellow needles; the *dibromide* melts at 142°; the *oxide*, $AsO(C_9H_{11})_3$, and *hydroxy-nitrate*, $OH\cdot As(C_9H_{11})_3\cdot NO_3$, melt at 129° and 147° respectively.

Trinitrotricumylarsine oxide, $AsO(C_6H_3Pr\cdot NO_2)_3$, produced by nitrating the tertiary arsine, crystallises in pale yellow needles and decomposes at 245°.

Tri-p-*cumylarsine sulphide*, prepared by leading hydrogen sulphide into a hot alcoholic solution of the oxide, melts at 149·5°.

Tri-p-*cumylmethylarsonium iodide* and the corresponding *ethiodide* melt at 103° and 138° respectively.

Trimesitylarsine, $As(C_6H_2Me_3)_3$, although obtained less readily than the preceding amines, is, nevertheless, produced with less difficulty than the corresponding phosphine; it crystallises from alcohol in prismatic needles and melts at 170°; the *hydroxy-chloride* forms white prisms and melts at 100°; the *dibromide* separates from alcohol in well-defined rhombic prisms and melts at 237°; the *oxide*, produced from the preceding halogen derivatives, melts at 203—204°.

Trimesitylmethylarsonium iodide, $As(C_9H_{11})_3MeI$, crystallises from alcohol in yellowish-red and from water in white prisms; it melts at 186°; the *chloride* and *platinichloride* melt at 192° and 237°.

[With A. Traegel.]—*Tri*-tert.*butylphenylarsine*, $As(C_6H_4{\cdot}CMe_3)_3$, is prepared by heating together bromo-*tert.*butylbenzene and arsenic chloride in a benzene solution; it melts at 235° and yields an *oxychloride* and *oxide*; the *dichloride* is stable. The *methiodide* decomposes at 125°, the quaternary *hydroxide* is obtained in rhombohedral crystals containing $4H_2O$.

[With H. Büschler.]—*Tri-a-naphthylarsine*, $As(C_{10}H_7)_3$, produced from α-bromonaphthalene, crystallises in slender prisms and melts at 252°; with excess of bromine or chlorine, it gives rise to the *tetrabromide*, $(C_{10}H_7)_3AsBr_4$, or the corresponding *tetrachloride* melting respectively at 180° and 144°.

The *hydroxy-bromide*, prepared by the action of bromine on a solution of the arsine in a mixture of benzene and alcohol, melts at 155° and yields the *hydroxide*, $As(C_{10}H_7)_3(OH)_2$, crystallising in needles with $2H_2O$, and melting above 300°.

The *oxide*, $AsO(C_{10}H_7)_3$, is obtained by heating the hydroxide at 110°; the sulphide and quaternary iodide could not be obtained.

Tri-β-naphthylarsine, prepared from β-bromonaphthalene, melts at 165° and is purified by the aid of its *mercurichloride*, which crystallises in leaflets and melts at 247°. The yield of the naphthylarsines is considerably less than that of the benzenoid derivatives.

Tri-β-naphthylarsine oxide is readily obtained in the anhydrous condition, the *sulphide*, formed by passing hydrogen sulphide into the alcoholic solution of the resinous *dibromide*, crystallises from this solvent in plates melting at 162°. G. T. M.

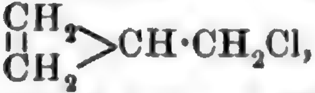
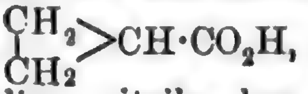
Organic Chemistry.

Hydrogenation of Ethylenic Hydrocarbons by the Method of Contact. By PAUL SABATIER and JEAN BAPTISTE SENDERENS (*Compt. rend.*, 1902, **134**, 1127—1130).—When hydrocarbons of the ethylene series up to C_8 are mixed with excess of hydrogen and passed over gently heated reduced nickel, they are converted into hydrocarbons of the methane series. If the temperature is below 160°, the product is practically pure, but above 200° there is partial disruption of the hydrocarbon chain, and paraffins of lower molecular weight are produced together with a small quantity of condensed products.

Reduced copper behaves similarly, but must be heated more strongly. It does not produce the hydrogenation of hydrocarbons which do not contain at least one unsubstituted CH_2 group. Styrene is converted into ethylbenzene. Limonene, at about 190°, is converted into a hydrocarbon, $C_{10}H_{18}$, which boils at 170° (corr.), and has a sp. gr. 0·827 at 0°/0°. In presence of nickel, the limonene is converted into hexahydrocymene, and is therefore an isomeride of menthene (compare Abstr., 1901, i, 195). C. H. B.

Acid Nature of Acetylene. By JEAN BILLITZER (*Zeit. physikal. Chem.*, 1902, **40**, 535—544).—The solubility of acetylene is increased by the addition of barium or ammonium hydroxide and diminished by the addition of potassium or sodium hydroxide, sodium sulphate, or sulphuric acid, the lowering being greatest for the sodium sulphate and least for the acid. The solubility of ethylene is similarly affected, but although the effect of the sodium sulphate is almost identical in the two cases, yet the alkalis produce a much greater decrease of solubility of ethylene than of acetylene. The author considers that this indicates an acid character of acetylene and the consequent formation of small quantities of salts. From the results, the dissociation of acetylene is estimated as about one-tenth of that of water, hence it follows that the reaction between calcium carbide and water must, at atmospheric pressure, be almost complete, or about 99·99 per cent.

L. M. J.

Trimethylenecarbinol and its Derivatives. By PAUL DALLE (*Bull. Acad. Roy. Belg.*, 1902, 36—79).—When trimethylenecarboxylonitrile (Abstr., 1899, i, 676) is reduced by sodium in alcohol, it furnishes the corresponding *amine*, a colourless liquid soluble in water, alcohol, or ether; this boils at 86° under 758 mm. pressure, and has a sp. gr. 0·8114 at 16°, n_D 1·4251 at 19°, and K 0·044. It is precipitated from its aqueous solution by potassium carbonate or hydroxide. The *hydrochloride* is white and hygroscopic, soluble in water or alcohol; the *platinichloride* forms golden-yellow lamellæ, slightly soluble in cold water. The hydrochloride, by treatment with sodium nitrite, furnishes *trimethylenecarbinol*, $\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>CH\cdot CH_2\cdot OH$, a colourless, slightly aromatic liquid, which boils at 125—126° under 756 mm. pressure, has a sp. gr. 0·9122 at 16°, n_D 1·43041, and is soluble in all ordinary solvents, but is precipitated from its aqueous solutions by addition of potassium carbonate or hydroxide. With hydrochloric acid, *trimethylenecarbinyl chloride*,  $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!>\!CH\cdot CH_2Cl$, is formed, a colourless, pleasant smelling liquid which boils at 85—86° under 756 mm. pressure, and has a sp. gr. 0·9647 at 16°. The corresponding *bromide* boils at 109—110° under 750 mm. pressure, and has a sp. gr. 1·387 at 16°; it does not combine with bromine, but with hydrogen bromide at 170° forms tetramethylene dibromide. The *iodide* is formed by the action of sodium iodide at 100° on either of the foregoing compounds dissolved in methyl alcohol. It is a colourless liquid, but becomes brown on exposure to air, boils at 135° under 760 mm. pressure, has a sp. gr. 1·725 at 16°, and is insoluble in water, but soluble in alcohol or ether. The *acetate* is a colourless liquid having an odour like that of ethyl acetate; it boils at 134° under 758 mm. pressure, has a sp. gr. 0·9605 at 16°, and is soluble in alcohol or ether but insoluble in water. The iso*butyrate* has similar properties, boils at 164° under 763 mm. pressure, has a sp. gr. 0·9378 at 16°, and is insoluble in water. The *trimethylenecarboxylate* is a slightly odorous, colourless liquid which boils at 191° and has a sp. gr. 0·9972 at 16°. Trimethylenecarboxylic acid,  $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!>\!CH\cdot CO_2H$, produced by alkaline hydrolysis of the corresponding nitrile, has *K* 0·00144; with phosphorus trichloride, it furnishes the *chloride*, a colourless, mobile liquid which boils at 119° under 760 mm. pressure, has a sp. gr. 1·185 at 17°; with ammonia, this is converted into the *amide*, which crystallises from ether, melts at 120°, and dissolves in alcohol but is insoluble in water. The iso*butyl ester* boils at 173—174° under 761 mm. pressure, and has a sp. gr. 0·9208 at 16°.

Methyltrimethylene derivatives in general have lower boiling points than the corresponding tetramethylene compounds, but the difference is not constant in value; compared with *iso*butyl compounds, the former have higher densities and conversely smaller mol. volumes, whilst the difference in boiling points of corresponding compounds is about 17° for mono-substituted derivatives such as *iso*butyl chloride (68·5°), and trimethylenecarbinyl chloride (85—86°), and about 24° to 28° for tri-substituted compounds such as the corresponding nitriles.

T. A. H.

Formation of αγ-Decylglycol from *iso*Valeraldehyde. By Hugo Rosinger (*Annalen*, 1902, **322**, 131—133).—The results already published by the author (Abstr., 1901, i, 669) completely contradict Nef's conclusions as to the formation of αγ-decylglycol from valeraldehyde and powdered sodium hydroxide (this vol., i, 7); the substance produced is, in reality, the mono*iso*valerate of this glycol. G. T. M.

Phosphomannitic Acid and Phosphomannitates. By L. Portes and G. Prunier (*J. Pharm. Chim.*, 1902, [vi], **15**, 457—466). —By heating mannitol and phosphoric acid together for several days in molecular proportion, *phosphomannitic* acid is formed. When purified, it is a gummy, colourless, very hygroscopic mass, and is dibasic, yielding both acid and normal salts. The *barium* salt, which forms a white, crystalline powder, is readily soluble in cold water, is partially decomposed by boiling water, and is insoluble in alcohol, ether, essential or fatty oils. Its solutions do not give the reaction of phosphoric acid with ammonium molybdate. The phosphomannitates of magnesium, iron, calcium, potassium, and sodium have also been prepared; with the exception of the magnesium salt, they are all amorphous.

A. F.

Ether Explosions. By E. von Neander (*Chem. Zeit.*, 1902, **26**, 336—337).—The residue obtained on evaporating the ethereal solution of a fat occasionally explodes violently during drying. It is found that when it has been kept for some months ether contains a quantity of active oxygen (estimated by the oxidation of hydriodic acid), equivalent to 0·24 per cent. of hydrogen peroxide. The active oxygen is possibly present in the form of ethyl peroxide, $(C_2H_5)_4O_3$ (Berthelot). On evaporation of such ether, a residue is obtained which does not explode; the presence of a fat is necessary. When an ethereal solution of a fat containing 0·14 per cent. of active oxygen was evaporated, the residue did not explode, but a vapour with a characteristic, unpleasant odour was given off. The evolution of this vapour was always noticed in those cases when an explosion occurred.

K. J. P. O.

Action of Phosphorus Chlorides on Organic Acids. Preparation of Trichloroacetyl Chloride. By Maurice Delacre (*Bull. Acad. roy. Belg.*, 1902, 189—202).—The action of phosphorus trichloride on organic acids has been represented by the following equations: (*a*) $3X{\cdot}CO_2H + 2PCl_3 = 3X{\cdot}COCl + P_2O_3 + 3HCl$ (Gal, *Rep. Chim. pur.*, 1863, **5**, 36); (*b*) $3X{\cdot}CO_2H + PCl_3 = 3X{\cdot}COCl + P(OH)_3$ (Wilde, *Bull. Acad. roy. Belg.*, **16**, 487); (*c*) $6X{\cdot}CO_2H + 3PCl_3 = 6X{\cdot}COCl + 3HPO_2 + 3HCl$ (Bechamp, *Compt. rend.*, 1885, **40**, 944; **41**, 23).

The author finds, as has already been observed by Thorpe (Trans., 1880, **37**, 186) in the case of acetyl chloride, that the preparation of trichloroacetyl chloride is best represented by equation (*a*), and points out that the latter also holds for the preparation of *iso*butyryl chloride (Burcker, *Ann. Chim. Phys.*, 1882, [v], **26**, 468) and trimethylacetyl chloride (Tissier, *ibid.*, 1893, [vi], **29**, 384), whence he concludes that it is generally applicable to this reaction; moreover, equation (*c*) is not in accordance with the amount of hydrogen chloride produced in practice, whilst equation (*b*) would seem to imply that the constitution of phosphorous acid is as written below, and that the two atoms of hydrogen in water do not possess the same function. $3H{\cdot}HO + PCl_3 = P(HO)_3 + 3HCl$.

T. A. H.

Attempt to Resolve Monochlorosulphoacetic Acid [into Optical Isomerides]. By Ch. Porcher (*Bull. Soc. Chim.*, 1902, [iii], **27**, 438—441).—The author has succeeded in resolving monochlorosulphoacetic acid into its optical isomerides by means of the cinchonine salt, although as yet he has not obtained them in a pure condition. The work is being continued. A. F.

Reactivity of Alkyloxy-acids. By Reinhold von Walther (*J. pr. Chem.*, 1902, [ii], **65**, 479—480).—Sodium methoxide and ethoxide react with ethyl chloroacetate in alcoholic solution; at the ordinary temperature, a crystalline, sodium compound is formed, but at 150° sodium chloride is eliminated and a product obtained which is probably a mixture of ethyl alkyloxyacetate, dialkyloxyacetoacetate, and alkyloxychloroacetoacetate. With chloroacetamide, sodium ethoxide and 2-methoxyphenoxide (guaiacyloxide) react in a similar fashion; in these cases, satisfactory yields of ethoxy- and of 2-methoxyphenoxy-acetamide are obtained, melting at 80° and 138° respectively.

These alkyloxy-esters, and yet more the aryloxy-esters, readily undergo condensation with other substances. Ethyl phenoxyacetate condenses with benzyl cyanide to form phenoxyacetylbenzyl cyanide, melting at 125°, and with acetophenone to form γ-benzoyl-α-phenoxyacetone, $OPh{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CPhO$, which will undergo further condensations, even with anthranilic acid. C. F. B.

Oxidised Oils. By Julius Lewkowitsch (*Analyst*, 1902, **27**, 139—145).—The results obtained in the examination of commercial blown Ravison rape oil, East India rape oil, and cotton-seed oil, solid linseed oil, and blown maize oil are tabulated. The oxidised acids contained in these oils were separated and investigated. They all showed considerably higher saponification values than acid values. That they are not saturated acids is shown by the comparatively high iodine numbers. The presence of lactones is indicated by the differences between the saponification and acid values, and lactonic compounds were actually separated from the oxidised acids. The other fatty acids, which had been freed from oxidised acids, also contained small quantities of lactones. The oxidised acids were soluble in water to a considerable extent. W. P. S.

The Origin and Nature of the Free Acid formed during Hübl's Reaction with Unsaturated Compounds. By Herbert Ingle (*J. Soc. Chem. Ind.*, 1902, **21**, 587—595).—The formation of the free acid produced during the action of iodine chloride solutions on unsaturated compounds is due to the action of water on the iodochlorides, and the quantity of the free acid is dependent on the structure of the compound and the amount of the water present. The nature of this acid was found to vary with the structure of the unsaturated compound. In using Wijs' reagent, the solution became dark brown in colour, probably due to the action of free hydriodic acid on iodine chloride, hydrogen chloride and iodine being formed. Some iodochlorides are reduced by potassium iodide, free iodine being liberated, causing a reduction in the apparent iodine absorption. This error may, in part, be avoided by the addition of more chloroform to dissolve the iodochlorides formed, and also by adding water to the test solution before potassium iodide. Iodine chloride is stated to be the active substance in "addition" and not hypoiodous acid. Some doubly linked carbon atoms, by the protecting influence of neighbouring groups, may be prevented from absorbing any halogen from a strongly acid Hübl's solution (Waller's), so that by determining the iodine value of a substance by Waller's, Wijs', and Hübl's methods, and the free acid formed during the latter reaction, the number of doubly linked atoms and their relative position in the molecule may be ascertained. In the methods ordinarily employed, substitution does not take place. W. P. S.

Glycerides of Fatty Acids with double Melting Point. By Hans Kreis (*Chem. Zeit.*, 1902, **26**, 384—385).—The author finds that the glycerides obtained by fractional crystallisation from ether of beef, mutton, and pork fat exhibit the phenomena of a double melting point, that is, they melt at a given temperature to a clear liquid, which at a higher temperature becomes turbid, and finally again clear. Hansen (*Chem. Zeit.*, 1902, **26**, 93) only observed a single melting point for these glycerides. K. J. P. O.

Halogen-substituted Malonic Acids and their Derivatives. By Max Conrad and H. Reinbach (*Ber.*, 1902, **35**, 1813—1821. Compare Willstätter, this vol., i, 342).—Chloromalonic acid can be quantitatively prepared by the action of the calculated quantity of sulphuryl chloride on malonic acid in solution in dry ether; the *lead* salt is a white precipitate, the *aniline* salt is crystalline and melts with evolution of carbon dioxide at 118°. Dichloromalonic acid was prepared in a similar manner by means of sulphuryl chloride; the *aniline* salt is crystalline and melts at 105° with evolution of carbon dioxide. Bromomalonic acid can easily be prepared by the action of bromine on an aqueous solution of sodium malonate or on an ethereal solution of malonic acid; the acid melts with evolution of carbon dioxide at 113° (compare Petrieff, this Journal, 1874, 787, and Abstr., 1878, 490); the *lead* salt is a white, crystalline precipitate; the *potassium* salt crystallises in slender needles. Dibromomalonic acid is very easily prepared by slowly adding bromine to malonic acid covered with aqueous hydrochloric or hydrobromic acid (compare Petrieff, *loc. cit.*, and Willstätter, *loc. cit.*); it melts and evolves carbon dioxide at 147°. The *lead* salt crystallises in long, slender needles which explode on heating; the *potassium* salt forms small needles, the *silver* salt is a white, crystalline precipitate. The *aniline* salt is crystalline, melts and evolves carbon dioxide at 113°, and in aqueous solution quickly becomes converted into aniline dibromoacetate.

Dibromomalonic acid can be nearly quantitatively converted into mesoxalic acid when it is heated with concentrated aqueous sodium hydroxide at 100°; sodium mesoxalate crystallises out on cooling. When sodium mesoxalate is treated with aniline in the presence of acetic or hydrochloric acid, the *aniline* salt of dianilinomalonic acid is formed; it melts and evolves carbon dioxide at 120°, and on boiling with water is converted into aniline and mesoxalic acid. In the preparation of methyl dianilinomalonate (this vol., i, 210), the addition of potassium acetate is recommended, as in the presence of this salt the methyl dibromomalonate is converted into methyl mesoxalate, which then reacts with aniline.

Methyl benzylbromomalonate is obtained when methyl benzylmalonate is brominated in ethereal solution, and crystallises in white prisms melting at 56°; on hydrolysis with sodium hydroxide, benzyltartronic acid (m. p. 147°) is obtained.

Methyl chlorobromomalonate crystallises in prisms melting at 37°.

K. J. P. O.

Monoethyl α-Anilinopyrotartarate Mononitrile [β-Anilino-β-cyanobutyrate] and its Products of Transformation. By GEORG SCHROETER and CARL KIRNBERGER (*Ber.*, 1902, **35**, 2078—2080).—Ethyl β-anilino-β-cyanobutyrate, prepared by Schiller-Wechsler's method (Abstr., 1885, 900) by the action of aniline on the cyanohydrin obtained from ethyl acetoacetate, was hydrolysed with sulphuric acid; the amide, $NHPh{\cdot}CMe(CO{\cdot}NH_2){\cdot}CH_2{\cdot}CO_2Et$, thus obtained melted at 109° (Schiller-Wechsler gave 125°) and is readily converted, with elimination of alcohol, into α-anilino-α-methylsuccinimide, which melts at 167° (Schiller-Wechsler, 150°), forms a crystalline hydrochloride, and is identical with the substance prepared by Strauss (Abstr., 1892, 1195) by the action of prussic acid on ethyl β-anilinocrotonate and subsequent treatment of the product with sulphuric acid. Attention is drawn to the fact that if this nitrile is treated with sulphuric acid without taking precautions as regards temperature, &c., a mixture of amide and imide is obtained, a fact which probably accounts for the conflicting results of previous authors.

K. J. P. O.

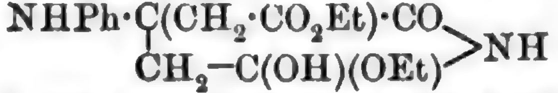
New Dimethylglutaric Acid. By EDMOND E. BLAISE (*Compt. rend.*, 1902, **134**, 1113—1115. Compare Abstr., this vol., i, 357).—In the action of phosphorus pentabromide on ethyl hydroxypivalate (*loc. cit.*), besides ethyl bromopivalate, an oily liquid is formed; the latter, when hydrolysed by potassium hydroxide, yields a *phosphate* of hydroxypivalic acid, $OH{\cdot}PO(O{\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2H)_2,H_2O$; it forms crystals losing H_2O at 100° and melting at 147°, behaves as a tribasic acid, forms a series of well-crystallised salts, and is very resistant to hydrolysis.

Ethyl bromopivalate condenses with ethyl potassiocyanoacetate with the production of an *ester*, $CO_2Et{\cdot}CMe_2{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et$, which boils at 166° under 16 mm. pressure. When this ester is hydrolysed and the substituted malonic acid thus obtained decomposed by heat, an acid is produced which can be purified in the form of its *anhydride*. The latter is a liquid boiling at 165—167° under 34 mm. pressure; with aniline, it yields an *anilide* melting at 131°, which, on heating, loses water, forming a *phenylimide* melting at 189°; with *p*-toluidine, a p-*toluidide* is formed melting at 138°. When the anhydride is boiled with water, an *acid*, $C_7H_{12}O_4$, is obtained, which melts at 74—75° and is not oxidised by heating with a mixture of nitric and sulphuric acids. From its method of formation, this acid should be αα-dimethylglutaric acid and identical with the acid obtained by the oxidation of camphor. This, however, is not the case. It is suggested that, possibly, in the preparation of the acid here described, a profound intramolecular change has taken place, and that the acid is an $\alpha\beta$-dimethylglutaric acid. K. J. P. O.

Oxidation of Glucosone to Trihydroxybutyric Acid. By Robert S. Morrell (*Proc. Camb. Phil. Soc.*, 1902, **11**, 340—341).—Glucosone (Trans., 1899, **75**, 345; 1900, **77**, 1219), when oxidised with bromine, gives trihydroxybutyric acid, which was identified in the form of the calcium salt. The calcium salt is very soluble in water and the solution gives, with lead acetate, a precipitate which is insoluble in dilute acetic acid.

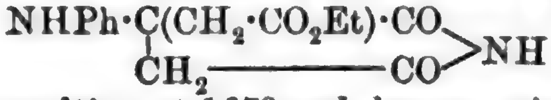
Calcium trihydroxybutyrate is reduced by hydriodic acid and phosphorus, giving butyric acid. J. McC.

Diethyl β-Anilinotricarballylic Acid Mononitrile and its Products of Transformation. By Georg Schroeter and Carl Kirnberger (*Ber.*, 1902, **35**, 2081—2084. Compare preceding page).—Ethyl anilacetonedicarboxylate combines with hydrogen cyanide forming a *cyanohydrin*, $NHPh\cdot C(CN)(CH_2\cdot CO_2Et)_2$, which forms crystals melting at 29°. When cautiously treated with concentrated sulphuric acid, the corresponding *amide* is obtained, to which is assigned the formula



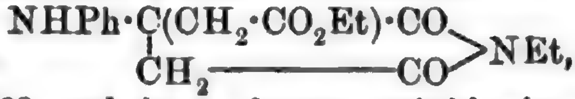
$$\begin{array}{l} NHPh\cdot C(CH_2\cdot CO_2Et)\cdot CO \\ CH_2-C(OH)(OEt) \end{array}\!\!>NH$$

; it forms crystals melting at 126°. If the cyanohydrin or the amide is treated with concentrated sulphuric acid for some time, an *imide* is formed with elimination of alcohol,



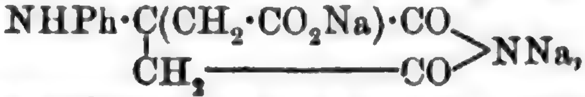
$$\begin{array}{l} NHPh\cdot C(CH_2\cdot CO_2Et)\cdot CO \\ CH_2\text{———————}CO \end{array}\!\!>NH$$

; this substance is a crystalline powder melting at 167° and has an acid reaction; its *acetyl* derivative melts at 178°. On treatment with ethyl iodide and sodium in alcoholic solution, an *ethyl* derivative is obtained,



$$\begin{array}{l} NHPh\cdot C(CH_2\cdot CO_2Et)\cdot CO \\ CH_2\text{———————}CO \end{array}\!\!>NEt$$

, forming large crystals melting at 68°, and is no longer soluble in alkalis. By the action of sodium on alcoholic solutions of the amide or imide, a *disodium* salt is formed,



$$\begin{array}{l} NHPh\cdot C(CH_2\cdot CO_2Na)\cdot CO \\ CH_2\text{———————}CO \end{array}\!\!>NNa$$

, which is very hygroscopic; on acidification of an aqueous solution, the corresponding *acid* is obtained; the latter begins to decompose at 57° and is only completely melted at 100°; the double *silver* salt, with silver nitrate, $C_{12}H_{11}O_4N_2Ag,AgNO_3$, is a white precipitate. K. J. P. O.

Dimethyl Hydrogen Citrate. By Georg Schroeter and Leonhard Schmitz (*Ber.*, 1902, **35**, 2085—2088. Compare preceding abstract).—*Dimethyl hydrogen citrate*, $C_3H_4(OH)(CO_2Me)_2\cdot CO_2H,H_2O$, can be prepared by one hour's boiling of a solution of citric acid in methyl alcohol containing a very small quantity of sulphuric acid; the ester is isolated as calcium salt; it crystallises in prisms or needles (from water), which melt, but not sharply, at 125—126°, and on heating decompose with loss of water and methyl alcohol, possibly forming an internal anhydride. The *calcium* salt is a white powder; the *silver* salt crystallises in leaflets; the *copper* salt forms blue crystals with $1H_2O$.

K. J. P. O.

Synthesis of Aldehydes. By Louis Bouveault and André Wahl (*Compt. rend.*, 1902, **134**, 1145—1147).—When nitro*iso*butylene is reduced by aluminium amalgam or by zinc powder and acetic acid, it yields *iso*butaldoxime, the corresponding hydroxylamine probably being formed as an intermediate product. Under similar conditions, nitrostyrene yields phenylacetaldoxime.

C. H. B.

The Acetal of Crotonaldehyde and its Conversion into Methyltriose. By Alfred Wohl and Franz Frank (*Ber.*, 1902, **35**, 1904—1910).—*β-Chlorobutyracetal*, $CHMeCl\cdot CH_2\cdot CH(OEt)_2$, prepared by the action of alcoholic hydrogen chloride on crotonaldehyde, boils at 70—71° under 12 mm. pressure and has a sp. gr. 0·975 at 17°. *Crotonacetal*, $CHMe{:}CH\cdot CH(OEt)_2$, prepared by distilling the preceding compound from potassium hydroxide, boils at 146—148°, and has a sp. gr. 0·8475 at 17°. *Methylglyceraldehyde acetal*,

$$OH\cdot CHMe\cdot CH(OH)\cdot CH(OEt)_2,$$

prepared by the action of 6 per cent. permanganate on the preceding compound, is a colourless, odourless, viscous liquid of bitter, burning taste, boils at 110—120° under 12 mm. pressure, and has a sp. gr. 1·0498 at 17°; unlike the two preceding compounds, which are insoluble, it is miscible with water in all proportions. *Methylglyceraldehyde*, $OH\cdot CHMe\cdot CH(OH)\cdot CHO$, prepared by the action of cold sulphuric acid on the acetal, is isolated by neutralising with baryta and evaporating the solution in a vacuum at 25—30°; it was obtained as a colourless syrup, of sweet, somewhat bitter taste, miscible with water and alcohol; for combustion, it was mixed with sand and dried over phosphoric oxide. The *phenylosazone*, $C_{16}H_{18}ON_4$, separates from hot benzene as a yellow, crystalline powder, sinters at 171°, melts at 171·5° (corr.), and decomposes at 190°. The *phenylbenzylhydrazone*, $C_{17}H_{20}O_2N_2$, is a colourless compound which crystallises from ether and melts at 116°.

β-Hydroxybutyracetal, $OH\cdot CHMe\cdot CH_2\cdot CH(OEt)_2$, is a colourless, mobile liquid, boils at 79—81° under 12 mm., and at 190—195° under 760 mm. pressure, dissolves in five parts of water, and cannot be oxidised to the corresponding ketone.

T. M. L.

Derivatives of Milk Sugar. By Rud. Ditmar (*Ber.*, 1902, **35**, 1951—1953).—Hepta-acetylchlorolactose, obtained by Bodart's method, melts, when recrystallised from ether, at a lower temperature (116—129°) than when precipitated from benzene by light petroleum; in the latter case, the crystals melt at 126—141°. When the acetyl compound is boiled in methyl alcoholic solution with silver carbonate, *hepta-acetylmethyl-lactoside*, $C_{12}H_{14}O_4(OAc)_7Me$, is obtained; it is precipitated from benzene solution by adding light petroleum as a crystalline mass, melts at 65—66°, reduces Fehling's solution, and is hydrolysed by an excess of baryta to lactose. By carefully boiling, however, with only a slight excess of the alkali, a *methyl-lactoside*, $C_{12}H_{21}O_{11}Me$, is obtained which melts at 171°.

Hepta-acetylbromolactose, $C_{26}H_{35}O_{17}Br$, is obtained by agitating carefully dried lactose with acetyl bromide for 8 hours in a flask from which moisture and light are excluded; it crystallises from ether in long prisms, melts at 138°, and has $[\alpha]_D$ +108·17 at 14° in chloroform; for bright blue light, it has $[\alpha]$ +130·87 at 14°. W. A. D.

The Initiative Action of Iodine and of other Oxidisers in the Hydrolysis of Starch and Dextrins. By F. E. HALE (*Amer. J. Sci.*, 1902, [iv], 13, 379—399).—In titrations with iodine, using starch as indicator, a reddish colour is often observed in place of the usual blue; in the titration, too, there is frequently a loss of iodine. If an absolutely pure and fresh starch solution be employed, no red colour is developed and there is no loss of iodine. Ordinary starch, however, contains two impurities, one of which gives a red colour with iodine, and the other, by the action of oxygen and potassium hydrogen carbonate, is transformed into that one which becomes red with iodine. The latter of the two (which is coloured blue with iodine) appears to be identical with the amidulin produced by the digestion of pure starch by saliva, whilst the former is erythrodextrin, which is the second salivary digestion product. The loss of iodine is attributed to the formation of erythrodextrin from the amidulin, the iodine acting in an oxidising capacity. That the loss of iodine is due to the starch is proved by the fact that hydrogen peroxide or potassium permanganate in presence of potassium hydrogen carbonate can oxidise starch so that starch iodide is not formed on the addition of iodine.

Experiments have been made with starch solutions prepared in different ways, and the loss of iodine with ordinary impure starch is quite apparent. The suggestion made by Girard (Abstr., 1887, 868) that potato starch absorbs three times as much iodine as rice starch has not been confirmed.

Attempts were made to isolate the impurities of starch, but these were not successful. It has, however, been shown that the compound which is coloured red by iodine can be produced by treatment of pure starch in potassium hydrogen carbonate solution with hydrogen peroxide or potassium permanganate. The impurity which is coloured blue with iodine, gives an iodide which is not precipitated by sulphuric acid, and differs, therefore, from starch iodide. The presence of erythrodextrin was recognised polarimetrically. The author discusses the mechanism of the hydrolysis by iodine. J. McC.

Conversion of Lactim Ethers into Lactams. By WILHELM WISLICENUS and HEINRICH KÖRBER (*Ber.*, 1902, 35, 1991—1992. Compare Abstr., 1900, i, 435; this vol., i, 211).—An almost theoretical yield of tetramethyluric acid is obtained when methoxycaffeine is heated at 200° for three hours. When ethoxycaffeine is heated at 240° for four hours, the product is 1 : 3 : 7-*trimethyl*-9-*ethyl*-2 : 6 : 8-*trioxypurine* melting at 197—198°. J. J. S.

New Method for the Preparation of Nitriles. By HANS BUCHERER (*Chem. Centr.*, 1902, i, 911; from *Zeit. Farben. Textilchem.*, 1902, 1, 70—72).—Nitriles may be prepared by the action of potassium cyanide on the additive compounds of Schiff's bases with sodium hydrogen sulphite. The latter compounds may be used in solution as prepared if an excess of the sulphite is avoided. A concentrated solution of potassium cyanide is added, and the mixture heated on the water-bath. The nitrile quickly separates in the form of an oil. E. W. W.

Methylindenes from Coal Tar. By JOHANNES BOES (*Ber.*, 1902, **35**, 1762—1764).—The coal tar fraction boiling at 200—210°, when freed from phenols and bases, is further purified by means of the picrate, and the hydrocarbon mixture thus obtained is fractionated and gives on analysis numbers corresponding with the formula $C_{10}H_{10}$. When boiled for some time with dilute nitric acid, the product yields a mixture of trimellitic and hemimellitic acids which are separated by means of their barium salts. Each of these tricarboxylic acids corresponds with two methylindenes, and in all probability the four possible isomerides are present in the mixture under examination. G. T. M.

Triphenylmethane and Concentrated Sulphuric Acid. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, **35**, 1754. Compare this vol., i, 381).—Triphenylmethane, when prepared by Friedel and Crafts' method, always contains traces of anthracene which are not readily removed by recrystallisation. It is to the presence of this impurity that the development of a yellow coloration with concentrated sulphuric acid is due, pure triphenylmethane dissolving to a colourless solution. G. T. M.

Triphenylmethane. By FRITZ ULLMANN (*Ber.*, 1902, **35**, 1811—1813. Compare preceding abstract).—Baeyer and Villiger (this vol., i, 380) have stated that triphenylmethane dissolves unchanged in sulphuric acid with a yellow coloration. The author finds that triphenylmethane is not dissolved by sulphuric acid, but only by fuming sulphuric acid, and then without any marked coloration; in the latter case, sulphonic acids are formed. When triphenylmethane is left for a long time under sulphuric acid, or when the hydrocarbon is heated with it at 80°, the sulphuric acid becomes yellow, but very little substance is dissolved. Further, if triphenylmethane containing a trace of triphenylchloromethane or triphenylcarbinol is shaken with sulphuric acid, the latter immediately becomes intensely yellow.
K. J. P. O.

Triphenylmethyl. IV. By MOSES GOMBERG (*Ber.*, 1902, **35**, 1822—1840. Compare Abstr., 1901, i, 77, 319, 638, 690).—Triphenylmethyl is best prepared by treating a solution of triphenylmethyl chloride in benzene with zinc; the solution immediately becomes yellow, and an additive compound of zinc chloride and triphenylmethyl chloride separates as an oil; after 5—15 days, the benzene is completely evaporated and the residue boiled with acetone; triphenylmethyl remains as a white, crystalline mass, which soon becomes yellow; in the dry state, it is fairly stable; its solutions are all yellow, and rapidly oxidise in the air, triphenylmethyl peroxide separating. Triphenylmethyl forms an *additive* compound with 1 mol. C_6H_6, which is obtained as large, colourless crystals when acetone is added to a solution of the hydrocarbon in benzene; it loses benzene when heated at 80—90°.

Triphenylmethyl immediately absorbs iodine, becoming converted into triphenylmethyl iodide; the additive compounds with ethyl acetate or benzene behave in a similar manner. On titrating the hydrocarbon with iodine in an organic solvent, it was found that only from 80—85 per cent. of the theoretical amount of iodine combined with the triphenylmethyl; some triphenylmethyl peroxide was always formed at the same time. From the solution of triphenylmethyl iodide thus obtained, triphenylmethylamine (m. p. 103°) was prepared by the action of ammonia. In a similar manner, *triphenylmethylethylamine* and *triphenylmethylpropylamine* were prepared; the former melted at 75—77°, the latter at 70—72°. *Triphenylmethylamylamine*, similarly obtained, is an oil which on boiling with dilute acids is converted into triphenylcarbinol; from the triphenylmethyl iodide, triphenylmethylaniline (m. p. 149—150°), triphenylmethyl-*o*-toluidine, and triphenylmethyl-*p*-toluidine were also prepared.

Triphenylmethyl bromide and iodide form pentabromo- and pentaiodo-additive compounds when the constituents are mixed in chloroform, benzene, or carbon disulphide solution.

Triphenylbromomethane pentabromide forms red crystals which lose bromine in the air; the *pentaiodide* forms well-defined crystals melting at 92°. *Triphenyliodomethane pentaiodide* crystallises in small prisms, melting at 90°, and is more stable than triphenylmethyl iodide (see below). By water, these perhaloids are converted into triphenylcarbinol, but by alcohol into triphenylmethane; in the presence of zinc dust or finely divided silver, alcohol converts them into triphenylmethyl ethyl ether. With acetyl chloride, the last mentioned substance does not yield triphenylmethyl acetate (Allen and Kölliker, Abstr., 1885, 655) but triphenylmethyl chloride. The author finds that triphenylmethyl acetate, prepared from triphenylmethyl chloride and silver acetate, melts at 87—88°.

In solution in ethyl acetate, the perhaloids are converted by zinc dust into triphenylmethyl.

Triphenylmethyl iodide can be prepared by mixing solutions of triphenylmethyl and iodine in warm petroleum, and forms large yellow crystals, which rapidly become brown with separation of iodine; it melts at 132°. When its solutions are exposed to the air, decomposition rapidly takes place, triphenylcarbinol, triphenylmethyl peroxide, and iodine being formed. Silver chloride converts triphenylmethyl bromide and iodide into triphenylmethyl chloride.

Most phenylhalogenmethanes readily form well crystallised additive compounds with metallic chlorides when the solutions of the constituents in ether benzene, ethyl acetate, &c., are mixed. By this means, a red, crystalline *additive* compound from antimony pentachloride and trichloromethyl chloride has been obtained. Tritolylmethyl chloride yields an orange *additive* compound with zinc chloride, a yellow crystalline *compound* with ferric chloride, and a red *compound* with mercuric chloride. Similar substances have been prepared from benzotrichloride, benzophenone chloride, and diphenylmethyl bromide.

K. J. P. O.

Basic Properties of Carbon. By Paul Walden (*Ber.*, 1902, **35** 2018—2031).—In order to investigate the basic nature of carbon in triphenylmethane derivatives, the electrical conductivities have been determined of solutions in sulphur dioxide of the following compounds: triphenylcarbinol, trimethylcarbinol, triphenylmethyl chloride and bromide, methyl iodide, allyl iodide, benzyl bromide, ethyl iodoacetate, *iso*butyl phenylbromoacetate, ω-bromostyrene, iodobenzene, α-bromonaphthalene, *tert.*butyl iodide, dipentene dihydrobromide, and dipentene dihydriodide.

For triphenylcarbinol, Δ was found to be 4·04, for *v* 85·59, and 6·23 for *v* 260, where Δ is expressed in reciprocal ohms, and *v* is the volume in litres containing one gram-mol. The solution in sulphur dioxide was pale yellow, and deposited yellow leaflets melting and decomposing at 152°. On evaporation of the solvent, colourless triphenylcarbinol was obtained melting at 158—159°. The conductivity of this substance is comparable to that of tertiary bases, quinoline, pyridine, &c., and of dimethylpyrone. Trimethylcarbinol gave Δ 0·0066 for *v* 20·5; the solution was colourless. The conductivity of triphenylcarbinol is therefore not due to the basic character of the oxygen. For triphenylmethyl chloride Δ was 8·34, for *v* 34·3, and 22·97 for *v* 284; monomethylammonium chloride gave Δ 10·15 for *v* 32, and Δ 22·76 for *v* 266; the former behaves as a true binary salt. The complex salt of triphenylmethyl chloride and stannic chloride, CPh_3SnCl_5, gave an intensely yellow solution with a conductivity comparable with that of potassium iodide:

	v.	Δ.	*v.*	Δ.
CPh_3SnCl_5	113	60·82	518	87·16
KI	128	61·7	512	92·7

Triphenylmethyl bromide formed an intensely yellow solution, the conductivity of which shows it to be one of the best electrolytes; thus for *v* 295, Δ = 126·4. Trimethylsulphonium chloride, and tetramethylammonium chloride and bromide have similar conductivities.

Of the other primary, secondary, and tertiary bromides and iodides investigated, only *tert.*butyl iodide, CMe_3I, gave a yellow solution in sulphur dioxide with a measurable conductivity; for *v* 112·5, Δ = 0·99, and for *v* 266, Δ = 1·41.

As dipentene and pinene show certain similarities with triphenylmethyl, both absorbing oxygen from the air and combining directly with water, it is suggested that these terpenes contain tervalent carbon; the conductivity of dipentene dihydriodide is also in agreement with this hypothesis; thus for *v* 121·4, Δ = 12·6, and for *v* 327·1, Δ = 16·5.

Attention is drawn to the fact that accompanying the change of acid character into basic character in the case of compounds of sulphur, oxygen, iodine, and nitrogen, there is a raising of valency; thus the acid bivalent sulphur of hydrogen sulphide becomes the basic quadrivalent sulphur of the sulphonium bases. From this point of view, acid characters should be associated with bivalent carbon. K. J. P. O.

Action of Arylamines on Benzene-*m*-sulphonic Chloride and Toluene-2 : 4-disulphonic Chloride. By JULIUS TROEGER and W. MEINE (*Ber.*, 1902, **35**, 1959—1960).—*Toluene*-2 : 4-*disulphonanilide*, $C_6H_3Me(SO_2 \cdot NHPh)_2$, separates from dilute alcohol in white crystals and melts at 189°. The o-*toluidide* forms pale violet crystals and melts at 170—171°. The m-*toluidide* melts at 138°. T. M. L.

Action of Phenylcarbimide on the Esters of some Oxy-acids. By EUGÈNE LAMBLING (*Bull. Soc. Chim.*, 1902, [iii], **27**, 441—451).—In the present communication, the author gives a number of supplementary details with regard to the properties of some of the compounds previously described (Abstr., 1899, i, 52). The phenylurethane of glycollic acid, $NHPh \cdot CO \cdot O \cdot CH_2 \cdot CO_2H$, when purified by crystallisation from chloroform, melts at 141°, passing at the same time into the internal anhydride. When boiled with an aqueous solution of sodium hydroxide, it decomposes with formation of carbonic and glycollic acids and aniline. The *sodium* salt, with $2H_2O$, crystallises in slender needles; the *ammonium* salt forms slender, anhydrous needles; the *barium* salt, which crystallises with $3H_2O$, is obtained as a felted mass of microscopic prisms; the *silver* salt forms slender needles. The lactam derived from the phenylurethane of glycollic acid crystallises in microscopic needles melting at 126°, is very sparingly soluble in cold water, and when boiled with it undergoes partial retransformation into the acid; it is also soluble in hot alcohol or benzene and in chloroform, but insoluble in ether. When heated with a solution of sodium carbonate, it passes into solution as the corresponding sodium salt. It has no basic properties. The author has also determined approximately the condition of equilibrium between the acid, anhydride, and water at the boiling point in the case of a 0·6 per cent. solution.

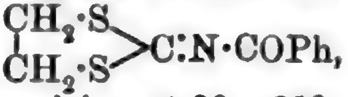
The phenylurethane of lactic acid melts at 142° and undergoes decomposition into aniline, carbon dioxide, and lactic acid when heated with water in a sealed tube at 150—160°. The *barium* and the *silver* salts crystallise in microscopic prisms. The lactam derived from the above acid melts at 142°.

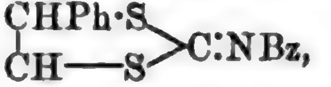
The *sodium* salt of the phenylurethane of phenylglycollic acid crystallises, with $3H_2O$, in slender needles very soluble in hot water; the *barium* salt, which also contains $3H_2O$, is obtained by double decomposition as a mass of microscopic needles, and the silver salt forms a mass of anhydrous, slender needles. A. F.

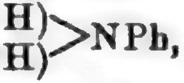
Thiocyanates and *iso*Thiocyanates [Thiocarbimides]. By HENRY L. WHEELER and HENRY F. MERRIAM (*J. Amer. Chem. Soc.*, 1902, **24**, 439—448. Compare Abstr., 1901, i, 514; this vol., i, 28, 366).—A mixture of methylene thiocyanate and thiobenzoic acid in benzene solution, when heated on the water-bath, deposits yellow crystals of *methylene dithiocarbamate*, $CH_2(CS \cdot S \cdot NH_2)_2$, which melts at 166°, and from the solution *methylene thiobenzoate benzoyldithiocarb-*

amate, $COPh\cdot NH\cdot CS\cdot S\cdot CH_2\cdot S\cdot COPh$, was isolated in the form of yellow prisms which melt at 138—139°. *Methylene benzoyldithiocarbamate*, $CH_2(S\cdot CS\cdot NH\cdot COPh)_2$, was also produced as yellow crystals melting at 130—131°, and hydrogen cyanide and carbon disulphide are simultaneously produced in the reaction.

Methylene thiolbenzoate, $CH_2(S\cdot COPh)_2$, prepared by treating potassium thiolbenzoate with methylene iodide, was obtained in the form of white needles, melting at 120°, which are insoluble in alkali.

A mixture of ethylene thiocyanate and thiobenzoic acid gives *ethylene dithiocarbamate* melting at 188—189°, and *benzoyliminomethylene ethylene disulphide*,  $\begin{matrix}CH_2\cdot S\\ |\\ CH_2\cdot S\end{matrix}>C\colon N\cdot COPh$, which crystallises in colourless, prismatic tablets melting at 80—81°; the constitution of the latter was proved by preparing it from thiocyanoethylsulphine hydrochloride and benzoyl chloride. It is insoluble in aqueous alkali but is decomposed by alcoholic potassium hydroxide.

Chloroethylene thiocyanate and thiobenzoic acid in benzene solution, when heated on the water-bath, give a white deposit of *iminomethylene ethylene disulphide hydrochloride*, which can be crystallised from alcohol or ether in thin plates which blacken at 200° and melt at 212°. In the same way, styrene thiocyanate gives crystals of *benzoyliminomethylene phenylethylene disulphide*,  $\begin{matrix}CHPh\cdot S\\ |\\ CH{-}{-}S\end{matrix}>C\colon NBz$, which melts at 135°. Trimethylene thiocyanate gives with thiobenzoic acid *trimethylene benzoyldithiocarbamate*, $CH_2(CH_2\cdot S\cdot CS\cdot NHBz)_2$.

Trimethylene thiocyanate, when heated on the water-bath with aniline and then precipitated with ether, gives tabular or prismatic crystals of *phenyl-ψ-trimethylenedithiobiuret*,  $CH_2<\begin{matrix}CH_2\cdot S\cdot C(NH)\\ CH_2\cdot S\cdot C(NH)\end{matrix}>NPh$, which melts at 173°. In the same way, styrene thiocyanate gives *ψ-phenylethylenephenyldithiobiuret*, which crystallises from a mixture of alcohol and ether in colourless plates melting at 205°.

m-*Xylene thiocyanate* is formed from *m*-xylene and potassium thiocyanate; it separates from alcohol in colourless crystals melting at 160—161°. With benzylidene chloride, potassium thiocyanate gives a mixture of benzaldehyde and ethyl thiocyanate. Methyl dibromohydrocinnamate, when treated with potassium thiocyanate, loses a mol. of bromine, and ψ-cyanogen disulphide and an unsaturated compound (methyl cinnamate) are formed. The same reaction takes place with other 2 : 3-dibromo-compounds. J. McC.

Conversion of Arylhydroxylamines into Diarylcarbamides. Arylmethylenehydroxylamines. By Eugen Bamberger and Henry Destraz (*Ber.*, 1902, **35**, 1874—1885).—Hydroxydiphenylformamidine, $NPh\colon CH\cdot NPh\cdot OH$, when treated with acetic anhydride at the atmospheric temperature, is converted into *s*-diphenylcarbamide, which in turn is partially converted into the acetyl derivative; the method by which the isomeric change takes place was not determined.

*Copper di-*p-*tolyloxyformamidine*, $Cu[O\cdot N(C_7H_7)\cdot CH\colon N\cdot C_7H_7]_2$, prepared by the action of anhydrous copper sulphate and sodium acetate on alcoholic di-*p*-tolylmethylenedihydroxylamine, separates from xylene in glistening prisms and melts at 263·5°.

Di-p-*tolyloxyformamidine hydrochloride*, $C_{15}H_{17}ON_2Cl$, separates as a white powder on adding hydrochloric acid to the copper salt suspended in hot acetone, and is precipitated from aqueous solution by concentrated hydrochloric acid in white, pearly needles melting at 198—199°. Acetic anhydride converts it into di-*p*-tolylcarbamide and its acetyl derivative. *Acetyldi*-p-*tolylcarbamide* crystallises from benzene in glistening, white needles, melts at 140°, and is hydrolysed by alcoholic potash into di-*p*-tolylcarbamide.

The *copper* salt of *di*-p-*chlorophenyloxyformamidine*,

$$C_6H_4Cl\cdot N(OH)\cdot CH{:}N\cdot C_6H_4Cl,$$

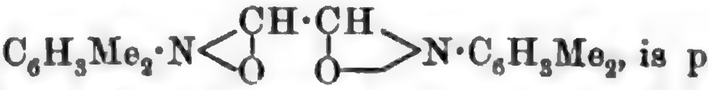
prepared from dichlorophenylmethylenedihydroxylamine, crystallises from xylene in short, brown, felted needles. When heated with acetic anhydride, it is converted into di-*p*-chlorophenylcarbamide and its acetyl derivative, the latter melting at about 160°.

Di-1 : 4 : 2-xylenemethylenedihydroxylamine,

$$CH_2[N(OH)\cdot C_6H_3Me_2]_2$$

(Abstr., 1900, i, 341), is reduced by aluminium amalgam to *p*-xylidine, and methyl-*p*-xylidine, $C_6H_4Me_2\cdot NHMe$. Anhydrous copper sulphate converts it into the *copper* salt of *di*-p-*xylyloxyformamidine*, $C_6H_3Me_2\cdot N{:}CH\cdot N(OH)\cdot C_6H_3Me_2$, which is a reddish-brown powder and does not melt at 300°; considerable quantities of azoxy-*p* xylene are also produced.

N-*Glyoxime*-p-*xylyl ether*,



$C_6H_3Me_2\cdot N\langle\overset{CH\cdot CH}{O\quad O}\rangle N\cdot C_6H_3Me_2$, is produced, together with *p*-xylidine and *p*-azoxyxylene, by heating di-*p*-xylylmethylenedihydroxylamine on a water-bath; it crystallises from alcohol or benzene in sulphur-yellow, silky, felted needles, melts at 204—205°, and by phenylhydrazine in acetic acid solution is converted into glyoxalosazone.

Di-1 : 3 : 4-*xylylmethylenedihydroxylamine*, $CH_2[N(OH)\cdot C_6H_3Me_2]_2$, from *as-m*-xylylhydroxylamine and formaldehyde, crystallises from benzene or from a mixture of chloroform and light petroleum in white, heavy crystals and melts at 128—129°; like other *o*-substituted methylene-ethers, it gives no colour with ferric chloride or copper acetate; it is decomposed by heat into *m*-xylyl-N-glyoxime, and by copper sulphate into dixylyloxyformamidine.

Di-o-*tolylmethylenedihydroxylamine*, $CH_2[N(OH)\cdot C_6H_4Me]_2$, separates from alcohol as a snow-white, crystalline powder, melts at 116—116·5°, and gives no coloration with ferric chloride or copper acetate; acetic anhydride converts it into glyoxime-N-phenyl ether or oxanilide (a product of the further action of acetic anhydride on the glyoxime ether), together with acetanilide, azoxybenzene, and *acetylphenylhydroxylamine*, $C_6H_5\cdot NAc\cdot OH$, which separates from light petroleum in glistening, flat needles, melts at 67—67·5°, and differs from formylphenylhydroxylamine mainly in that it does not form a sparingly soluble copper salt.

Formylphenylhydroxylamine, $C_6H_5\cdot N(OH)\cdot CHO$ (this vol., i, 279), is best prepared from phenylhydroxylamine and anhydrous formic acid, and by cautiously heating with phosphoric oxide is converted into phenylcarbimide. T. M. L.

Etherification of Pyrogallol. By WILHELM HIRSCHEL (*Monatsh.*, 1902, **23**, 181—198. Compare *Monatsh.*, 1889, **10**, 150).—When treated with potassium hydroxide and ethyl bromide, pyrogallol yields chiefly the triethyl ether, accompanied by an oil from which ethylcatechol diethyl ether, ethylpyrogallol triethyl ether, and a substance boiling at 149—150° under 15 mm. pressure, apparently isomeric with the latter, have been isolated.

Ethylcatechol diethyl ether boils at 121° under 15 mm. pressure. When boiled with hydriodic acid, it is hydrolysed to *ethylcatechol*, a mobile, colourless liquid, soluble in alcohol, insoluble in water, which distils unchanged under reduced pressure, does not solidify at $-10°$, becomes brown on exposure to air, gives with ferric chloride a dirty green colour changing through intense violet to ruby-red on addition of sodium carbonate, forms a voluminous precipitate with lead acetate, and reduces ammoniacal silver nitrate in the cold. When boiled with acetic anhydride and sodium acetate, it forms a white *acetyl* derivative melting at 53°. With fuming nitric acid, it yields *dinitroethylcatechol diethyl ether* crystallising from alcohol in long, greenish needles which melt at 83°. The alcoholic mother liquor yields a derivative of lower melting point, probably the *mononitro*-compound. The action of bromine on ethylcatechol diethyl ether in glacial acetic acid solution and of nitric acid on the oil so formed leads to the formation of *bromonitroethylcatechol diethyl ether*, which crystallises in long needles, melts at 78°, and with fuming nitric acid yields *bromodinitroethylcatechol diethyl ether* melting at 65—66°.

Ethylpyrogallol triethyl ether boils at 143° under 15 mm. pressure, and with fuming nitric acid yields *dinitroethylpyrogallol triethyl ether*, which crystallises from alcohol in colourless needles, melts at 51°, and becomes dark yellow on exposure to light. The alcoholic mother liquor yields a substance which melts at 45°, and is probaby the *mononitro*-derivative. The action of sulphuric acid on pyrogallol triethyl ether leads to the formation of the *sulphonic acid* which crystallises from water in nodules. An attempt to liberate the sulphonic acid from its lead salt by means of sulphuric acid resulted in hydrolysis to pyrogallol triethyl ether. When treated with an excess of bromine in acetic acid solution, the triethyl ether yields *tribromopyrogallol triethyl ether*, which melts at 38—39°. *Bromopyrogallol diethyl ether*, formed by warming pyrogallol triethyl ether with 1 mol. of bromine in acetic acid solution, crystallises in needles and melts at 103—104°. On addition of 1 mol. of bromine to the triethyl ether in cold acetic acid solution and addition of water, an oil is formed which is converted by nitric acid into *bromonitropyrogallol triethyl ether*, crystallising from alcohol in thin needles and melting at 104°. As this bromonitro-derivative is also obtained by bromination of Schiffer's nitropyrogallol triethyl ether (Abstr., 1892, 715), it must have the constitution $[(OEt)_3 : Br : NO_2 = 1 : 2 : 3 : 4 : 5]$. With fuming nitric acid, it yields *bromodinitropyrogallol triethyl ether*, which melts at 74°. G. Y.

Hexahydro-*o*-toluic Acid. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1902, 26, 335).—*Hexahydro-o-toluic acid* [2-*methyl*cyclo*hexanecarboxylic acid*], obtained when *o*-toluic acid is reduced by means of amyl alcohol and sodium, melts at 50° and boils at 242°; the *anilide* melts at 148°. At the same time, a second isomeric acid is formed, identical with that obtained by Perkin and Goodwin (Trans., 1895, 67, 119); the latter boils at 236—237° and forms an *anilide* melting at 66°.

K. J. P. O.

Nitration with Ethyl Nitrate. By WILHELM WISLICENUS and ANTON ENDRES (*Ber.*, 1902, 35, 1755—1762).—Ethyl nitrate, in the presence of sodium or sodium ethoxide, condenses with compounds containing a reactive methylene group to yield *iso*nitro-derivatives, $CXY\colon NO_2Na$.

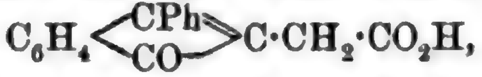
Ethyl sodium iso*nitrophenylacetate*, $CPh(\colon NO_2Na)CO_2Et$, prepared by condensing ethyl phenylacetate and ethyl nitrate with sodium suspended in dry ether, was not obtained in a state of purity. Its existence was demonstrated by hydrolysing the crude product with concentrated sodium hydroxide solution when the sodium derivative of *iso*nitrophenylmethane was produced. The new compound resembles nitrophenylmethane in forming a labile *iso*-modification. This is shown by acidifying the aqueous solution of its sodium salt, extracting with ether, and adding ferric chloride; a brownish-red coloration is developed, which disappears slowly after a time, and very rapidly on warming. The property of developing the coloration is recovered by reconverting the substance into its metallic derivative and repeating the preceding experiment.

iso*Nitrobenzyl cyanide*, obtained by the condensation of benzyl cyanide and ethyl nitrate in the presence of sodium or sodium ethoxide suspended in dry ether, is isolated in the form of its *sodium* derivative, $CN\cdot CPh\colon NO_2Na$, a compound separating from alcohol as a brown, crystalline mass; it gives a deep green coloration with ferric chloride, and with silver nitrate yields the *silver* derivative, $CN\cdot CPh\colon NO_2Ag$, a pale yellow, crystalline powder decomposing energetically on heating. When freshly liberated from a solution of its sodium derivative, the nitro-compound probably has the *iso*nitro-configuration, for it develops a red coloration with ferric chloride; it is, however, very unstable and rapidly changes into a resinous product. The nitro-compound, when distilled in steam, yields a small amount of stilbene dicyanide, and on reduction with zinc dust and sodium hydroxide gives rise to *iso*nitrosobenzyl cyanide, the yield being 70 per cent. of the theoretical; hydrolysis with concentrated alkali hydroxide solution leads to the production of sodium *iso*nitrophenylmethane, and affords a ready means of preparing this substance.

The action of alcoholic hydrogen chloride on the nitro-compound results in the formation of stilbene dicyanide and nitrous acid; the presence of ethyl nitrophenylacetate was not indicated. An attempt to prepare a methyl derivative from sodium *iso*nitrobenzyl cyanide with methyl iodide at 100° led to the production of *iso*nitrosobenzyl cyanide.

G. T. M.

Indoneacetic Acids. I. 3-Phenyl-1-indone-2-acetic Acid and 3-Phenyl-1-hydrindone-2-acetolactone. By HANS STOBBE and WALTHER VIEWIG (*Ber.*, 1902, **35**, 1727—1737).—The principal product of the action of cold concentrated sulphuric acid at 10° on γ-diphenylitaconic acid is 3-*phenyl*-1-*indone*-2-*acetic acid*,

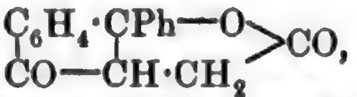


$$C_6H_4{<}\begin{matrix}CPh\\CO\end{matrix}{>}C\cdot CH_2\cdot CO_2H,$$

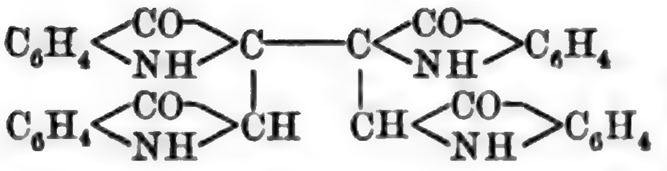
which crystallises from benzene in small, lustrous, orange-yellow prisms and melts at 167·5°; the *barium* salt, $(C_{17}H_{11}O_3)_2Ba,3H_2O$, forms orange-red needles, the *calcium* salt is reddish-yellow, and the *silver* salt yellow and sensitive to light. The *semicarbazone*, $C_{18}H_{15}O_3N_3$, crystallises from alcohol in yellow needles and melts and decomposes at 218—220°. The *ethyl* ester, $C_{19}H_{16}O_3$, of the acid, obtained by adding diethyl diphenylitaconate dissolved in light petroleum to concentrated sulphuric acid is dimorphous; it crystallises from light petroleum in dull, triclinic prisms melting at 81·5°, and from alcohol and benzene in silky, rhombic plates melting at 77°; when melted, the triclinic form is converted into the rhombic one. The same ethyl ester is obtained, along with the phenylindoneacetic acid, by the action of sulphuric acid on monoethyl diphenylitaconate,

$$CPh_2{:}C(CO_2Et)\cdot CH_2\cdot CO_2H,$$

a result which can only be explained by assuming that the alcohol originally eliminated in forming the indoneacetic acid esterifies the latter. That an indone acid, and not a naphthalene derivative, is formed by the action of sulphuric acid on γ-diphenylitaconic acid, is held to be proved from the following considerations: (1) the yellow colour of the products—a phenylketodihydronaphthoic acid would be colourless; (2) oxidation of the acid with alkaline potassium permanganate gives *o*-benzoylbenzoic acid; (3) with bromine, two isomeric, colourless *monobromolactones*, $C_{17}H_{11}O_3Br$, are obtained; an α-ketodihydronaphthoic acid would give a stable dibromide; (4) concentrated mineral acids convert the indoneacetic acid into an isomeric saturated *lactone*, the identity of this compound with the lactone next described is uncertain.

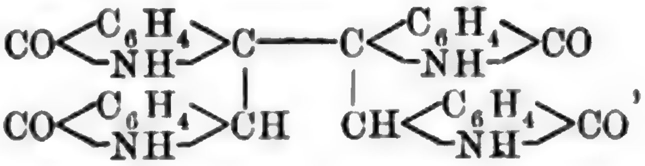
3-*Phenyl*-1-*hydrindoneacetolactone*,  $\begin{matrix}C_6H_4\cdot CPh-O\\CO-CH\cdot CH_2\end{matrix}{>}CO$, obtained as a bye-product of the action of concentrated sulphuric acid on γ-diphenylitaconic acid, separates from carbon disulphide in white, triclinic crystals, melts at 119—120°, and is converted by bases into the isomeric phenylindoneacetic acid; the *semicarbazone*, $C_{18}H_{15}O_3N_3$, crystallises from alcohol in colourless, woolly needles and melts and decomposes at 256—261°. W. A. D.

Indigotin and Indigo-red. By WILHELM VAUBEL (*Chem. Centr.*, 1902, i, 936; from *Zeit. Farben. Textilchem.*, 1902, 1, 39—45. Compare Abstr., 1901, i, 714).—When indigotin and indigo-red are reduced intermediate products,



$$\begin{array}{rcl}\mathrm{C_6H_4}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{C} & \text{——} & \mathrm{C}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{C_6H_4}\\ | & & | \\ \mathrm{C_6H_4}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{CH} & & \mathrm{CH}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{C_6H_4}\end{array}$$

and



$$\begin{array}{rcl}\mathrm{CO}<\substack{\mathrm{C_6H_4}\\ \mathrm{NH}}>\mathrm{C} & \text{——} & \mathrm{C}<\substack{\mathrm{C_6H_4}\\ \mathrm{NH}}>\mathrm{CO}\\ | & & | \\ \mathrm{CO}<\substack{\mathrm{C_6H_4}\\ \mathrm{NH}}>\mathrm{CH} & & \mathrm{CH}<\substack{\mathrm{C_6H_4}\\ \mathrm{NH}}>\mathrm{CO},\end{array}$$

are formed respectively. These compounds differ from the colourless end-products in forming red solutions when dissolved in alcoholic solutions of alkalis; the reduction product of indigo-red has a deeper colour than indigo-red itself. Attempts to prepare optically active indigo-white failed. By the action of potassium bromide and potassium bromate on indigotin suspended in sulphuric acid or dissolved in chloroform, *m*-bromoisatin is formed together with a *compound*,

$$C_{16}H_8O_2N_2Br_2,$$

which melts at 125° and is soluble in ether or chloroform.

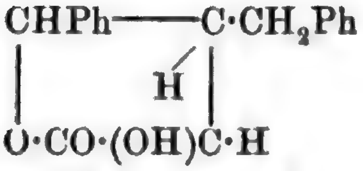
E. W. W.

Isomeric *cis-trans-α*-Keto- and *α*-Hydroxy-lactones and Selection in the Formation of Compounds with Several Asymmetric Carbon Atoms. By Emil Erlenmeyer, jun. (*Ber.*, 1902, **35**, 1935—1943. Compare Erlenmeyer and Lux, Abstr., 1898, i, 668).—Similar results are obtained on reducing α-oxy-β-phenyl-γ-benzylbutyrolactone and α-oxy-γ-phenyl-β-benzylidenebutyrolactone as were given formerly by α-oxy-βγ-diphenylbutyrolactone (*loc. cit.*).

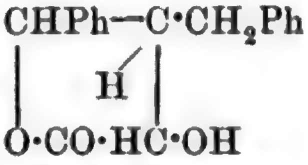
α-Oxy-β-phenyl-γ-benzylbutyrolactone, $\mathrm{CH_2Ph{\cdot}CH}<\substack{\mathrm{CHPh}\\ \mathrm{O{-}CO}}>\mathrm{CO}$, when reduced with sodium amalgam, gives a mixture of two stereoisomeric *hydroxy-lactones*, $\begin{array}{lcl}\mathrm{CHPh} & \text{——} & \mathrm{CH{\cdot}CH_2Ph}\\ \mathrm{H{\cdot}C(OH){\cdot}CO{\cdot}O} & & \end{array}$ and $\begin{array}{l}\mathrm{CHPh{-}CH{\cdot}CH_2Ph}\\ \mathrm{OH{\cdot}CH{\cdot}CO{\cdot}O}\end{array}$; the former is the more soluble in chloroform, crystallises in needles, and melts at 113°, the latter separating in prisms and melting at 153°. These substances are accompanied by an *acid*, $C_{17}H_{16}O_3$, melting at 161°, which, by boiling mineral acids, is converted into an isomeric *acid* melting at 128°.

α-Oxy-γ-phenyl-β-benzylidenebutyrolactone, $\mathrm{CHPh{:}C}<\substack{\mathrm{CHPh}\\ \mathrm{CO{\cdot}CO}}>\mathrm{O}$, on reduction with zinc dust and acetic acid, gives two racemic *stereoisomerides*, which can be denoted by the formulæ $\mathrm{CH_2Ph{\cdot}CH}<\substack{\mathrm{CHPh}\\ \mathrm{CO{\cdot}CO}}>\mathrm{O}$ and $\mathrm{H{\cdot}C(CH_2Ph)}<\substack{\mathrm{CHPh}\\ \mathrm{CO{\cdot}CO}}>\mathrm{O}$; the one more soluble in water melts at 134°, the other melting at 137°; the latter alone is obtained on condensing benzylpyruvic acid with benzaldehyde. Along with the stereoisomerides, an *acid*, $C_{17}H_{16}O_3$, melting at 143° is obtained, which, by boiling with mineral acids, is converted into an isomeric acid melting at 97°.

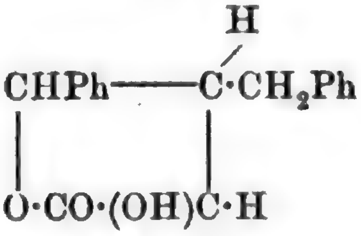
Each of the stereoisomeric keto-lactones gives two racemic hydroxy-lactones when reduced by sodium amalgam; the two forms obtained from the keto-lactone melting at 134° melt at 109—110° and 155—156°, and those from the lactone melting at 137° at 110° and 155°; the four forms seem to be distinct, and can be represented by the formulæ:



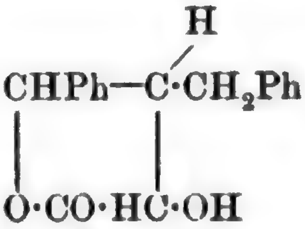
M. p. 109—110°.



M. p. 155—156°.



M. p. 110°.



M. p. 155°.

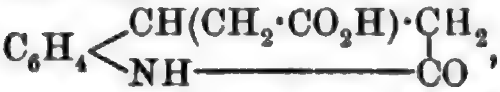
Starting with the racemic form (+ –) of an unsaturated compound containing one asymmetric carbon atom, reduction has given rise to the two racemic forms $\left(\begin{smallmatrix}+&-\\+&-\end{smallmatrix}\right)$ and $\left(\begin{smallmatrix}+&-\\-&+\end{smallmatrix}\right)$, corresponding with a derivative containing two asymmetric carbon atoms; the four hydroxy-lactones, which contain three such asymmetric carbon atoms, correspond with the racemic forms:

$$\begin{pmatrix}+&-\\+&-\\+&-\end{pmatrix} \qquad \begin{pmatrix}+&-\\+&-\\-&+\end{pmatrix} \qquad \begin{pmatrix}+&-\\-&+\\+&-\end{pmatrix} \qquad \begin{pmatrix}-&+\\+&-\\+&-\end{pmatrix}$$

W. A. D.

Nitrated Phenylglutaric Acids and their Reduction Products. By Georg Schroeter and Hans Meerwein (*Ber.*, 1902, **35**, 2073—2078).—On nitrating β-phenylglutaric acid, a mixture of *o*- and *p*-nitro-derivatives is obtained; these are separated by extracting the mixture with boiling water, in which only the ortho-derivative is soluble. β-p-*Nitrophenylglutaric acid* crystallises in needles melting at 240°; its *methyl* ether melts at 65°. The o-*nitro-acid* crystallises in pale yellow leaflets melting at 174°; its *methyl* ester forms white needles melting at 41°. β-2:4-*Dinitrophenylglutaric acid*, prepared by nitrating the *p*-nitro-acid, crystallises in long, yellow needles melting at 177°; its *methyl* ester forms large crystals melting at 50°. β-p-*Aminophenylglutaric acid*, obtained by reducing the corresponding nitro-derivative with ammonium sulphide or alcoholic stannous chloride, crystallises in needles melting and decomposing at 217°; the *methyl* ester forms white leaflets melting at 63°; the *copper* salt, with $2H_2O$, forms a pale green powder, the *acetyl* derivative leaflets melting at 103°.

On reducing *o*-nitrophenylglutaric acid with ammonium sulphide, an acid was formed which crystallised and melted at 204·5°, its *methyl* ester crystallised in prisms melting at 65·5°; with alcoholic stannous chloride, on the other hand, *hydrocarbostyril-4-acetic acid*,



$$C_6H_4<\begin{matrix}CH(CH_2\cdot CO_2H)\cdot CH_2\\ NH\text{————————}CO\end{matrix}$$

, is obtained, crystallising in silky needles melting at 183°; its *methyl* ester melts at 111°; the *copper* salt is a pale green precipitate; the *silver* salt is soluble in hot water.

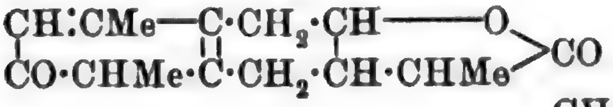
When 2:4-dinitrophenylglutaric acid is reduced with ammonium sulphide, *β-4-amino-2-nitrophenylglutaric acid* is formed, crystallising in reddish-yellow leaflets which melt and decompose at 206·5°.

7-*Nitrohydrocarbostyril-4-acetic acid* is obtained if alcoholic stannous chloride is used as the reducing agent; it forms yellow crystals melting at 185·5°; its *methyl* ester crystallises in golden-yellow needles melting at 125°, is soluble in alkalis, and forms a reddish-yellow *silver* salt. If the dinitro-acid is reduced with excess of stannous chloride, *β-2:4-diaminophenylglutaric acid* is formed; its *copper* salt crystallises with $1H_2O$.

K. J. P. O.

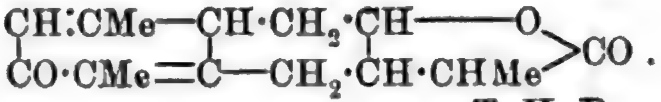
Yellow Santonin (Chromosantonin). By CLEMENTE MONTEMARTINI (*Gazzetta*, 1902, **32**, i, 325—366).—The author has made an extended study of the properties of the yellow compound formed by the action of sunlight on santonin and of its derivatives. The transformation is unaccompanied by change in weight, and the yellow compound has the same percentage composition and the same molecular weight as unaltered santonin; the change is a complete one and not merely superficial. Chromosantonin yields derivatives distinguishable from those of santonin by their different rotatory powers and by their yellowish tint. Chromosantonin and some of its coloured derivatives are transformed into the corresponding colourless forms by repeated crystallisation. Those derivatives of chromosantonin which contain the same number of carbon atoms, and during the formation of which a change takes place in the molecular nucleus, as, for example, santonous and santonic acids, are identical with those prepared from santonin. Chromosantonin retains the ketonic and lactonic functions of santonin, but in presence of reducing agents, such as stannous chloride, it reacts much more readily than santonin but gives the same products as the latter. Chromosantonin is more easily oxidised than santonin, and the products obtained from the two compounds are quite different.

The author discusses the various structural formulæ possible for the chromosantonin molecule, which he considers to have one of the two following constitutions:



$$\begin{matrix}CH{:}CMe—C\cdot CH_2\cdot CH\text{———}O\\ CO\cdot CHMe\cdot C\cdot CH_2\cdot CH\cdot CHMe\end{matrix}>CO$$

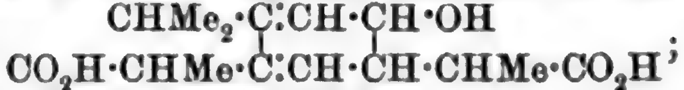
and



$$\begin{matrix}CH{:}CMe—CH\cdot CH_2\cdot CH\text{———}O\\ CO\cdot CMe{=}C—CH_2\cdot CH\cdot CHMe\end{matrix}>CO.$$

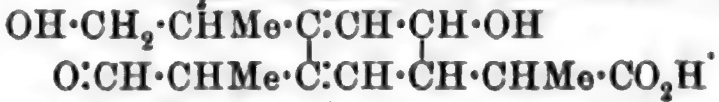
T. H. P.

Constitution of Photosantonic and *iso*Photosantonic Acids. By LUIGI FRANCESCONI and L. VENDETTI (*Gazzetta*, 1902, **32**, i, 281—322).—The authors discuss the work of previous investigators on these two acids and from a consideration of such work and of some new results obtained by them, they arrive at the following new formulæ for the acids: Photosantonic acid,



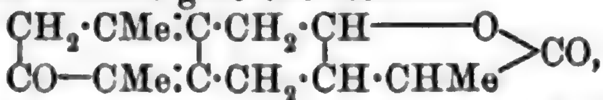
$$\begin{array}{l}\mathrm{CHMe_2{\cdot}C{:}CH{\cdot}CH{\cdot}OH}\\ \mathrm{CO_2H{\cdot}CHMe{\cdot}C{:}CH{\cdot}CH{\cdot}CHMe{\cdot}CO_2H}\end{array};$$

*iso*photosantonic acid,



$$\begin{array}{l}\mathrm{OH{\cdot}CH_2{\cdot}CHMe{\cdot}C{:}CH{\cdot}CH{\cdot}OH}\\ \mathrm{O{:}CH{\cdot}CHMe{\cdot}C{:}CH{\cdot}CH{\cdot}CHMe{\cdot}CO_2H}\end{array}.$$

To santonin, the authors give the formula



$$\begin{array}{l}\mathrm{CH_2{\cdot}CMe{:}C{\cdot}CH_2{\cdot}CH{-}{-}O}\\ \mathrm{CO{-}CMe{:}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe}\end{array}\!\!>\mathrm{CO},$$

and they explain the formation of photosantonic and *iso*photosantonic acids by the action of light as due to the transference of the double linking of the nucleus of the santonin molecule containing the carbonyl group to the other nucleus to which the lateral propionic chain is attached; in the new compound thus formed, the first-named nucleus is then severed and the elements of water taken up, the lactones of photosantonic and *iso*photosantonic acids being thus obtained. The yellow colour which is temporarily formed during the transformation of santonin into these two lactones, but which disappears when the change is complete, is assumed to be due to the formation of the intermediate compound just referred to.

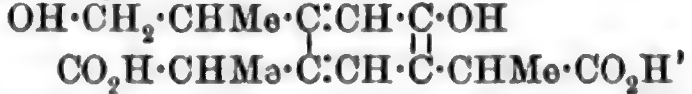
Besides repeating work previously published, the authors have obtained the following new compounds.

iso*Photosantonic acid oxime*, $C_{15}H_{22}O_4{:}NOH$, separates in small, rhombohedral crystals which soften at 130°, melt at 151° and are soluble in acetic acid and to a slight extent in alcohol or ether; it has $[\alpha]_D$ +170·30°. When boiled with acetic anhydride and acetyl chloride, it yields a condensation product, $C_{30}H_{36}O_5N_2$, separating from chloroform in small scales which decompose at 279° and are slightly soluble in ethyl acetate or ethylene bromide.

iso*Photosantonolactone oxime*, $C_{15}H_{20}O_3{:}NOH$, crystallises from ethyl acetate in shining needles melting and decomposing at 220°. Its *acetyl* derivative, $C_{17}H_{23}O_5N$, separates from acetic anhydride solution in square, blunt-angled crystals melting at 170° and is soluble in alcohol, ethyl acetate, or acetic anhydride.

iso*Photosantonolactone phenylhydrazone*, $C_{15}H_{21}O_4{:}N_2HPh$, separates from ethyl acetate in long, straw-coloured crystals which melt and decompose at 239°.

Hydroxydehydroisophotosantonic acid,



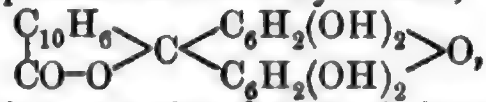
$$\begin{array}{l}\mathrm{OH{\cdot}CH_2{\cdot}CHMe{\cdot}C{:}CH{\cdot}C{\cdot}OH}\\ \mathrm{CO_2H{\cdot}CHMe{\cdot}C{:}CH{\cdot}C{\cdot}CHMe{\cdot}CO_2H}\end{array},$$

prepared by oxidising *iso*photosantonic acid with acid permanganate solution, is deposited from ethyl acetate in shining, prismatic crystals melting at 283—284° and is slightly soluble in alcohol, benzene, chloroform, or solutions of alkali or alkaline earth hydroxides. Its *acetyl* derivative, $C_{17}H_{22}O_7$, separates from ethyl acetate in prismatic crystals which melt at 251° and are soluble in alcohol or chloroform; it has $[\alpha]_D$ +58·13°. The *barium* salt, $C_{15}H_{28}O_6Ba$, was prepared and analysed.

T. H. P.

Dihydroxyfluoresceins and Dihydroxyeosins. By CARL LIEBERMANN and F. WÖLBLING (*Ber.*, 1902, **35**, 1782—1788).—The *dihydroxy-*

fluorescein of 1 : 2-naphthalenedicarboxylic acid,



$$\begin{matrix}C_{10}H_6\\ |\\ CO{-}O\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_2(OH)_2\\ C_6H_2(OH)_2\end{matrix}\!>\!O,$$

is prepared by heating together for 2—3 hours at 205—210° the anhydride of naphthalene-1 : 2-dicarboxylic acid and hydroxyquinol, and crystallising the crude product from alcohol ; it separates as a reddish-brown powder readily soluble in glacial acetic acid. The substance dissolves in solutions of the alkali hydroxides and ammonium carbonate, in the latter case, the red solution has a yellowish-green fluorescence ; it is sparingly soluble in boiling water, but dissolves in cold concentrated sulphuric acid to a yellow solution, which, on warming, becomes blue and yields a cœrulean blue derivative on dilution with water, this product being also soluble in alkali hydroxides.

The *dibromodihydroxyfluorescein* of 1 : 2-naphthalenedicarboxylic acid, $C_{24}H_{12}O_7Br_2$, produced by the action of bromine on the preceding compound dissolved in glacial acetic acid, crystallises from acetone in white needles melting at 85°. These colourless needles probably consist of an unstable compound with acetone of crystallisation ; on drying at 60° they become golden-yellow and then melt and decompose at 220—230°.

Dihydroxydimethoxyfluorescein, $C_{22}H_{16}O_9$, prepared from hemipinic anhydride and hydroxyquinol, separates from its alcoholic solution on adding water as a light red powder.

The *dihydroxyfluorescein*, $C_{19}H_{11}O_7N$, of quinolinic acid is obtained by heating quinolinic anhydride and hydroxyquinol at 150° (compare Graebe and Philips, Abstr., 1893, i, 670 ; Philips, Abstr., 1895, i, 572).

The *dihydroxyfluorescein* of diphenyltetrenecarboxylic acid is a brick-red powder prepared by melting together hydroxyquinol and the anhydride of diphenyltetrenecarboxylic acid at 220—230° ; it is soluble in glacial acetic acid, alcohol, or acetone, but insoluble in water, chloroform, or benzene; the alcoholic solution has a greenish-yellow fluorescence. The compound yields a well-defined, crystalline bromo-derivative.

The preceding substituted fluoresceins and eosins have been examined spectroscopically, and also as dyeing agents for mordanted textile fabrics with the view of ascertaining the effect of substitution on the tinctorial properties of the compounds. The spectroscopic results are tabulated ; the account of the dyeing experiments cannot be suitably abstracted.

G. T. M.

Action of *p*- and *m*-Nitrobenzaldehyde on Vanillin. By M. Rogoff (*Ber.*, 1902, **35**, 1961—1964).—p-*Nitrobenzylidenedivanillin*, $NO_2\cdot C_6H_4\cdot CH[C_6H_2(OH)(OMe)\cdot CHO]_2$, prepared by heating vanillin and *p*-nitrobenzaldehyde with zinc chloride, is precipitated in flakes on diluting a solution in acetone, is very sparingly soluble in most solvents, but dissolves in alkalis to a yellow solution, melts and decomposes at 276° (corr.), and reduces cold ammoniacal silver and hot Fehling's solution. The *hexa-acetate*, $NO_2\cdot C_6H_4\cdot CH[C_6H_4(OAc)(OMe)\cdot CH(OAc)_2]_2$, crystallises from much alcohol in slender, microscopic prisms, is readily soluble in most solvents, and melts at 205·5—207° (corr.).

m-*Nitrobenzylidenedivanillin* crystallises from hot dilute acetic acid in microscopic needles, melts and decomposes at 266·5° (corr.), reduces cold ammoniacal silver solutions only slowly, and hot Fehling's solution not at all. The *hexa-acetate* crystallises from alcohol in small prisms and melts at 154—155° (corr.). The bis-*phenylhydrazone*, $C_{35}H_{31}O_6N_5$, crystallises from hot dilute alcohol and melts and decomposes at 226° (corr.). T. M. L.

Benzoin. By Emil Knoevenagel and J. Arndts (*Ber.*, 1902, **35**, 1982—1990. Compare Zinin, *J. pr. Chem.*, 1866, **98**, 495; Limpricht and Jena, *Annalen*, 1870, **155**, 89; Klinger, Abstr., 1886, 888).—Benzoin is not readily acted on by aqueous potassium hydroxide even when warm and as concentrated as 30 per cent., provided air is excluded. More concentrated alkali (60—80 per cent.), even when air is not present, converts the benzoin into benzyl alcohol and benzoic acid. The best yield of benzyl alcohol, namely, 40 per cent. of the benzoin, is obtained when the alcohol is removed as quickly as formed by the aid of steam at 180—200°, or when the temperature is only raised to 120—130° and the reaction not allowed to proceed for too long a time. Prolonged action of the alkali at both high and low temperatures lessens the yield of alcohol, and secondary products, namely, stilbene hydrate and hydrobenzoin, are produced together with a substance, $C_{18}H_{18}O_2$, probably diethylcarbobenzonic acid (Limpricht and Schwanert, *Annalen*, 1870, **155**, 66). It would appear that these secondary products are due to the reducing action of the alcohol on the benzoin, the alcohol itself being oxidised to benzaldehyde, which is then converted by the alkali into benzyl alcohol and benzoic acid.

The chief products formed when benzoin is heated with solid potassium hydroxide are benzyl alcohol, deoxybenzoin, benzhydrol, benzyldeoxybenzoin, and benzoic and benzilic acids. The action of alkali on other ketones is being investigated. J. J. S.

Action of Nitric Acid on Quinone. By Fausto Sestini (*Gazzetta*, 1902, **32**, i, 322—324).—It was stated by Schoonbroodt in 1861 that the action of nitric acid on quinone yields oxalic and picric acids. The author, however, has not been able to find any trace of picric acid in the products of this reaction. When concentrated nitric acid is employed, small quantities of aromatic nitro-compounds are obtained, whilst with dilute acid the quinone is not completely oxidised.

T. H. P.

Hystazarin. By Carl Liebermann and W. Hohenemser (*Ber.*, 1902, **35**, 1778—1781. Compare this vol., i, 475).—The properties ascribed to hystazarin by Lagodzinski and Lorétan (Abstr., 1895, i, 232) do not correspond with those indicated by Liebermann and Schöller (Abstr., 1888, 1203). The dimethyl ether of hystazarin, produced from dimethoxybenzoylbenzoic acid, is not readily hydrolysed with concentrated hydrochloric acid at 110° for 5—6 hours; the reaction is, however, rendered complete by treatment with 40 parts of the acid at 200—205° for 10—20 minutes. The purification of hystazarin by repeated extraction with hot toluene is absolutely essential, for, during hydrolysis at the higher temperature, this substance becomes more or less transformed into alizarin, and after $2\frac{1}{2}$ hours the yield of the latter compound is about 50 per cent.

The alternative method of synthesising hystazarin from catechol and phthalic anhydride leads to the production of six parts of this compound mixed with one part of alizarin.

Alizarin, although scarcely acted on by concentrated sulphuric acid at 200°, is slowly oxidised to purpurin when the temperature is raised to 225°. G. T. M.

Derivatives of Anthraquinone obtained in the Action of Sodium Peroxide on Aloins and their Haloid Derivatives. By Eugène Léger (*Compt. rend.*, 1902, **134**, 1111—1113).—When a hot solution of barbaloin or *iso*barbaloin is treated with sodium peroxide, the liquid becomes deep red, and, on acidification, aloe-emodin (m. p. 224·5—225·5°, corr.) is precipitated in both cases; this substance has the composition of a trihydroxymethylanthraquinone, and is identical with the substance obtained by Oesterle (Abstr., 1899, i, 538). The author names this substance *iso*hydroxymethylchrysasin. When heated with zinc dust, it yields a hydrocarbon melting at 208·7° (corr.), which, on oxidation, gives an anthraquinonecarboxylic acid; the latter can be converted into anthraquinone.

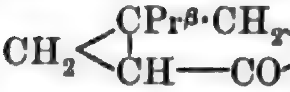
Chlorobarbaloin and chloro*iso*barbaloin are converted by sodium peroxide into *tetrachloroisohydroxymethylchrysasin*, $C_{15}H_6O_5Cl_4$, crystallising in reddish-orange needles and melting at 229—231° (corr.); on heating with acetic anhydride and acetyl chloride, a *triacetyl* derivative is obtained which crystallises in pale yellow needles melting at 270—271° (corr.). The corresponding *tetrabromo*-compound is obtained from bromobarbaloin and crystallises in cinnabar-red needles melting at 264—266° (corr.).

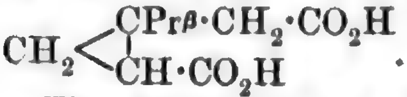
By the action of sodium peroxide on nataloin or homonataloin, *methylnataloe-emodin* (dihydroxymethoxymethylanthraquinone), $C_{16}H_{12}O_5$, is obtained, which crystallises in yellowish-orange needles melting at 238° (corr.); it dissolves in alkalis with a yellowish-orange and in sulphuric acid with a violet coloration; an anthraquinonecarboxylic acid can be obtained from it. When heated with hydrochloric acid at 170°, it is converted into a *compound*, $C_{15}H_{10}O_5$ (?), which crystallises, with $1H_2O$, in dark reddish-orange needles melting at 220·5° (corr.), and gives with sodium hydroxide a violet, and with sulphuric acid a gooseberry-red, coloration. This compound is named nataloe-emodin.

Optically active substances having the properties of pentoses are formed, together with the compounds just described, by the action of sodium peroxide on the aloins. K. J. P. O.

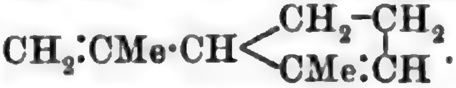
Decomposition of Cevadine [Veratrine] in Alcoholic Solution by Hydrogen Chloride. By Paul Horst (*Chem. Zeit.*, 1902, **26**, 334).—When hydrogen chloride is passed into an alcoholic solution of veratrine, ethyl tiglate (b. p. 151—152°) is obtained, which on hydrolysis yields tiglic acid (m. p. 62—63°). The tiglic acid is not produced from the angelic acid first formed, as the latter, under the same conditions, is not converted into tiglic acid (compare Wright and Luff, Trans., 1878, **33**, 338; Ahrens, Abstr., 1890, 1448; Freund and Schwarz

Abstr., 1899, i, 464). Some of these authors have suggested that angelic acid is the first product of the hydrolysis of veratrine, and is subsequently converted into tiglic acid. K. J. P. O.

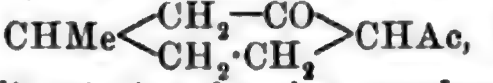
Sabinenes. By Friedrich W. Semmler (*Ber.*, 1902, **35**, 2045—2049. Compare Abstr., 1900, i, 452).—When sabinene ketone,  $CH_2<\begin{array}{l}CPr^{\beta}\cdot CH_2\\ CH—CO\end{array}>CH_2$, is oxidised with an alkaline solution of bromine, there is obtained, together with bromoform, an acid melting at 142—143°, which proved to be tanacetonedicarboxylic acid,

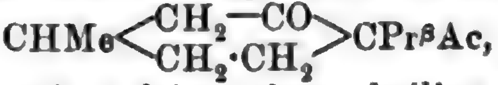


$CH_2<\begin{array}{l}CPr^{\beta}\cdot CH_2\cdot CO_2H\\ CH\cdot CO_2H\end{array}$.

The semicarbazone of sabinene ketone does not regenerate the ketone when warmed with 25 per cent. sulphuric acid, but a liquid *hydrocarbon*, C_9H_{14}, is formed, which boils at 165—166°, and has a sp. gr. 0·839 at 20°, and n_D 1·4732. This substance is regarded as having the constitution  $CH_2{:}CMe\cdot CH<\begin{array}{l}CH_2-CH_2\\ CMe{:}CH\end{array}$.

On reducing sabinene ketone with sodium and alcohol, *sabinene alcohol*, $C_9H_{16}O$, is obtained; in attempting to oxidise the alcohol again to the ketone, the hydrocarbon just described was mainly obtained. K. J. P. O.

Synthesis of Menthone. By Georges Leser (*Compt. rend.*, 1902, **134**, 1115—1116).—The potassium derivative of 4-acetyl-1-methyl-3-*cyclo*hexanone,  $CHMe<\begin{array}{l}CH_2—CO\\ CH_2\cdot CH_2\end{array}>CHAc$, condenses with *iso*propyl iodide in alcoholic solution, forming *acetylmenthone*,



$$CHMe<\begin{array}{l}CH_2—CO\\ CH_2\cdot CH_2\end{array}>CPr^{\beta}Ac,$$

which is a liquid with a faint odour, boiling at 133—135° under 13 mm. pressure, and has a sp. gr. 0·967 at 15° and n_D 1·45737. When boiled with methyl alcoholic potassium hydroxide, menthone is obtained boiling at 207—208°; the *semicarbazone*, $C_{11}H_{21}ON_3$, melts at 179—180°, and the oxime at 98—99°. K. J. P. O.

Ethereal Oils. By Schimmel & Co. (*Chem. Centr.*, 1902, i, 1058—1060; from *Geschäftsber.*, April, 1902. Compare Abstr., 1901, i, 394).—Oil of citronella from Ceylon does not contain citronellol but *d*-citronellol has been isolated from the Java oil by treatment with phthalic anhydride. The citronellol obtained from the phthalate boils at 103° under 5 mm. pressure, and has the sp. gr. 0·8618 at 15°, $[\alpha]_D$ +2°17′, and n_D 1·45704 at 22°.

The presence of pinene has not yet been detected in lemon oil (compare Burgess and Child, this vol., ii, 232).

The oil prepared from *Eucalyptus pulverulenta* has a sp. gr. 0·9217 at 15°, $[\alpha]_D$ +1°4′, and is soluble in 2 volumes of 70 per cent. alcohol.

In one sample of oil of lavender, adulteration with benzoic acid was detected.

Oil of cloves contains methyl *n*-amyl ketone and methyl benzoate, the former boils at 151—153° and has a sp. gr. 0·8223 at 15°. The sp. gr. of eugenol containing water was found to be 1·0725, that of the anhydrous compound being 1·0716 at 15°.

Cinnamon oil from Ceylon contains methyl *n*-amyl ketone, furfuraldehyde, pinene, cymene, benzaldehyde, nonaldehyde, cuminaldehyde, linalool, and caryophyllene,—hydrocinnamaldehyde and linaloyl *iso*butyrate are also probably present in the oil.

Oil from *Artemisia variabilis* from Reggo has the odour of petitgrain oil, a sp. gr. 0·9115 at 15°, $[\alpha]_D$ – 9°20′, and is partially soluble in alcohol; its saponification number is 15·5, whilst that of the acetyl derivative is 49·1.

Oil from the leaves, branches, and fruit of the mandarin tree or "petitgrain mandarinier" of the South of France has an odour like that of neroli and an intense blue fluorescence; it has a sp. gr. 1·005 at 15°, rotatory power + 7°19′, saponification number 159·1, and is soluble in 9 volumes of 80 per cent. alcohol.

Oil of toona-wood from Nicaragua has a sp. gr. 0·9212 at 15°, $[\alpha]_D$ – 46°50′, and consists mainly of cadinene. Cadinene hydrochloride melts at 116·5—117° and has $[\alpha]_D$ – 1°36′ in 5 per cent. ethereal solution. Cadinene, prepared from the hydrochloride, boils at 128—130° under 4 mm. pressure and has a sp. gr. 0·9244 at 15° and $[\alpha]_D$ – 99°6′. Pure safrole solidifies at 11·2° and has a sp. gr. 1·1058—1·1060 at 15° and n_D 1·53917. E. W. W.

Oil of Coffee. By Ernst Erdmann (*Ber.*, 1901, **35**, 1846—1854).—The oil is best obtained by distilling roasted coffee with slightly superheated steam, and may readily be separated into an indifferent portion, amounting to about 58 per cent. of the whole, and an acid portion which amounts to 42 per cent. of the whole and consists of a valeric acid, probably α-methylbutyric acid. The indifferent portion contains about 50 per cent. of furfuryl alcohol, together with a number of phenols. The fraction which contains the characteristic odorous constituent of the oil boils at 93° under 13 mm. pressure and contains 9·71 per cent. of nitrogen. It is only obtained in extremely small quantity, the yield being about 0·89 gram from 65 kilos. of coffee, and possesses in a marked degree the delicate aroma of the coffee. The aroma of coffee is produced when caffetannic acid, caffeine, and cane sugar are gently heated together, but not when any one of these constituents is omitted. A. H.

Constituents of Galanga Oil. By J. Schindelmeiser (*Chem. Zeit.*, 1902, **26**, 308).—The oil boiled at 170—275°, had a sp. gr. 0·91 at 20°, a rotatory power – 2°27′ in a 100 mm. tube, and n_D 1·4663 at 20°. Pinene, cineol, and possibly cadinene are present in the oil; in the fraction 230—240°, a new hydrocarbon is found, the *hydrochloride* of which, $C_{15}H_{24},2HCl$, crystallises in leaflets, is optically inactive, and melts at 51°. K. J. P. O.

Resina Pini from Siebenbürgen (from Picea Vulgaris). By Alexander Tschirch and M. Koch (*Arch. Pharm.*, 1902, **240**, 272—287. Compare Abstr., 1901, i, 91).—The resin contained 20 per cent. of woody and other impurities; purified from these, it had acid and saponification number 126 and iodine number 54·4. By distilling the resin, formic, acetic, and succinic acids were obtained. A small quantity of a *bitter-substance* is present in the resin.

From an ethereal solution of the resin 1 per cent. aqueous ammonium carbonate extracted *picipimarinic acid*, $C_{12}H_{20}O_2$, which is amorphous, melts at 132—135°, and has acid and saponification number 288, corresponding with monobasicity, and iodine number 64·4, corresponding with the formation of a monoiodo-derivative.

One per cent. aqueous sodium carbonate solution then extracted a mixture of acids. From a solution of these in a mixture of methyl and ethyl alcohols, piceapimaric acid crystallises identical with that obtained from Jura turpentine; it is optically inactive and has acid and saponification number 187·5, corresponding with monobasicity, and iodine number 35·4, corresponding with the formation of a monoiodo-derivative. From the mother liquor, *α- and β-picipimarolic acids*, $C_{18}H_{28}O_2$, were isolated; these are amorphous and melt at 90—96° and 88—94° respectively; they have acid and saponification number 204, corresponding with monobasicity, and iodine number 46·35, corresponding with the formation of a monoiodo-derivative; their lead salts are respectively insoluble and soluble in alcohol.

Aqueous potassium hydroxide extracted nothing from the remaining ethereal solution, but a reddish *colouring-matter* separated at the junction of the two liquids.

When the ether was distilled off and the residue distilled with steam, an *essential oil* came over which boiled at 175—180° and had the sp. gr. 0·870, whilst an amorphous substance of an indifferent character, *picoresen*, $C_{19}H_{30}O$, remained behind. A little of this resen separated when the ethereal solution of the resin was extracted with ammonium carbonate.

In 100 parts of the (purified) drug there were contained: picipimarinic acid, 3; piceapimaric acid, 2; α- and β-picipimarolic acids, 47; essential oil, 30; picoresen, 15; bitter-substance (succinic acid), colouring matter, water and impurities, 3. C. F. B.

West Indian Sandalwood Oil. By Ernst Deussen (*Arch. Pharm.*, 1902, **240**, 288—293. Compare Abstr., 1900, ii, 579).—By suitable treatment of the oil, chiefly fractionation, oils were obtained which had respectively: boiling point under 26 mm. pressure, 153—154°, 155—156° (260—261° and 257—259° under atmospheric pressure), 150—143°, 139—141°; sp. gr. 0·925, 0·914, 0·903, 0·902 at 15°, and specific rotation, $[\alpha]_D$ $+54°$, $+(11—16°)$, $-2\frac{1}{2}°$, $-5\frac{1}{4}°$. The first forms with hydrogen chloride a crystalline hydrochloride melting at 117—118°, and is probably *r*-cadinene; the second may be galipene; the last two are possibly identical, and may be caryophyllene or guajene.

C. F. B.

Caoutchouc. II. By Carl O. Weber (*Ber.*, 1902, **35**, 1947—1951).—Purified Para rubber dissolved in benzene is converted by nitrosyl chloride, produced by the interaction of amyl nitrite and acetyl chloride, into a stiff jelly which soon decomposes, evolving gas and giving a solution of apparently unchanged rubber. Nitrogen peroxide, evolved from lead nitrate, precipitates from a solution of caoutchouc in benzene, a brownish-yellow, amorphous powder, which is very soluble in acetone, and is precipitated from it by water in the form of a bright yellow mass having the composition $C_{10}H_{16}O_4N_2$. Balata and guttapercha give compounds of the same composition, but that obtained from the former is only sparingly soluble in acetone. These substances easily dissolve in alkalis; the *sodium* derivative, $C_{10}H_{15}O_4N_2Na$, was obtained as a brown, flocculent mass by dissolving the substance in concentrated methyl alcoholic sodium methoxide and diluting with absolute alcohol; the corresponding *silver* derivative, $C_{10}H_{15}O_4N_2Ag$, is precipitated by silver nitrate from an aqueous solution of the sodium compound as a brownish jelly. W. A. D.

Catechin. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1901, **35**, 1867—1869).—Catechin appears to have the formula $C_{15}H_{14}O_6,4H_2O$. The penta-acetyl compound, $C_{15}H_9O(OAc)_5$, can be readily prepared by the direct action of acetic anhydride and sodium acetate, and was previously described by Liebermann and Tauchert (Abstr., 1881, 52) as diacetylcatechin. *Tetramethylcatechin*,

$$C_{15}H_9O(OMe)_4{\cdot}OH,$$

prepared by the action of methyl sulphate on catechin, crystallises in needles melting at 142—143°. Pure sulphuric acid yields a yellow solution with a green fluorescence, but if nitrous acid be present a deep reddish-violet coloration is produced. *Acetyltetramethylcatechin* crystallises in colourless needles melting at 92—93°. The tetramethyl compound is converted by oxidation with cold chromic acid solution into *trimethylcatechone*, $C_{18}H_{18}O_7$, which crystallises in orange-coloured needles and melts and decomposes at 210°. A. H.

Furfuryl Alcohol. By ERNST ERDMANN (*Ber.*, 1901, **35**, 1855—1862).—Furfuryl alcohol is best prepared by a modification of Schiff's method (*Ber.*, 1886, **19**, 2154), furfuraldehyde being gradually added to aqueous sodium hydroxide and the product distilled with steam. It forms a colourless liquid of characteristic odour and bitter taste, boils at 68—69° under 10 mm. and 170—171° under 758 mm. pressure, and has a sp. gr. 1·1351 at 20°/20°. The pure substance mixes with water in all proportions, but the solution gradually separates into two layers; the nature of this decomposition has not yet been ascertained. The pure compound, moreover, does not form the compound with aniline which was obtained by Schiff. When brought into contact with aldehydes and hydrochloric acid, a bluish-green coloration is produced, and this reaction is also given with a pine wood splinter moistened with hydrochloric acid. Furfuraldehyde, however, produces with it a bluish-violet coloration.

Furfuryl diphenylcarbamate, $NPh_2{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}C_4OH_3$, obtained by heating the alcohol with diphenylcarbamide chloride and pyridine, forms lustrous, faintly yellow needles melting at 97·5—98°. The corresponding *furfuryl carbamate*, $NH_2{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}C_4H_3O$, crystallises in slender needles melting at 50°. It is accompanied by another compound which melts and decomposes at 170°.

The physiological effect of the alcohol on rabbits, investigated by E. Harnack, is that respiration is paralysed, the lethal dose being 0·5—0·6 gram per kilo. A. H.

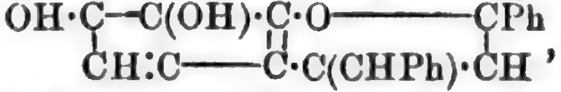
Naphthafurfuran from Coal Tar. By JOHANNES BOES (*Zeit. öffentl. Chem.*, 1902, 8, 151—152. Compare Abstr., 1897, i, 526; 1900, i, 650).—After being freed from phenols and bases, the fraction of coal tar boiling at 282—292° is alternately redistilled, treated with picric acid, and the picrate decomposed by steam. On cooling, the purified fraction, boiling at 282—286°, deposits β-naphthafurfuran (m. p. 60—61°, b. p. 284—286°). The liquid part of the fraction is α-naphthafurfuran, which has a sp. gr. 1·1502 at 15°, and boils at 282—284°.

The yields are 2 grams of β- and 0·5 gram of α-naphthafurfuran from 2 kilos. of the original fraction boiling at 282—292°. G. Y.

Polyvalent Oxygen. By PAUL WALDEN (*Ber.*, 1902, 35, 1764—1772. Compare this vol., i, 169).—This communication contains a short summary of the bibliography of quadrivalent oxygen, a discussion of the univalent and sexavalent character of this element, and an account of electrical experiments indicating that dimethylpyrone is not only a basic, but also an acidic, substance.

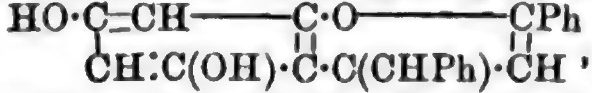
The electrical conductivity of dimethylpyrone in hydrazine hydrate solution at 0° varies from 15·2 to 23·9 units acccording as the concentration diminishes from 1 gram-mol. in 100 litres to the same amount in 420 litres. A solution of a true binary salt, namely, tetraethylammonium iodide, having a similar concentration has only double the conductivity, and this result serves to show that a salt has been produced between the hydrazine and the dimethylpyrone. G. T. M.

1 : 4-Benzopyranol Derivatives from Phenylacetylacetophenone and Trihydric Phenols and Orcinol. By CARL BÜLOW and HANS GROTOWSKY (*Ber.*, 1902, 35, 1799—1810. Compare Abstr., 1901, i, 400, 559, 603; this vol., i, 112—113).—The *hydrochloride* of 7 : 8-*dihydroxy-2-phenyl-4-benzylidene*-1 : 4-*benzopyranol*,

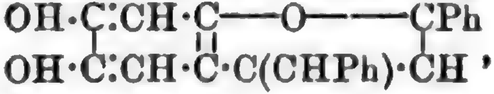


$$\begin{array}{l}\mathrm{OH{\cdot}C{-}C(OH){\cdot}C{\cdot}O{-\!-\!-\!-}CPh} \\ \quad\ \mathrm{CH{:}C{-\!-}C{\cdot}C(CHPh){\cdot}CH}\end{array},$$

is prepared by passing hydrogen chloride into a mixture of phenylacetylacetophenone and pyrogallol dissolved in acetic acid; it crystallises with $1H_2O$ in reddish-brown, lustrous needles decomposing at 245°, and dissolves in concentrated sulphuric acid with a yellow coloration; this solution does not fluoresce. The *picrate* crystallises in reddish-brown, lustrous leaflets which sinter on heating and melt at 193°. On heating the hydrochloride with sodium acetate in acetic acid solution, the *diacetyl* derivative of the benzopyranol is obtained; it crystallises in pale yellow needles, which soften at 156° and melt and decompose at 160°. The *dibenzoyl* derivative, prepared from the hydrochloride, crystallises in yellow needles melting and decomposing at 178°. The *dimethoxy*-derivative, prepared by heating the hydrochloride with sodium and methyl iodide in methyl alcoholic solution, crystallises in long, yellow needles melting and decomposing at 141—143°.

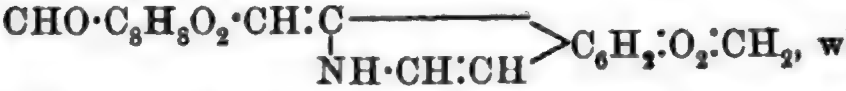
The *hydrochloride* of 5 : 7-*dihydroxy-2-phenyl-4-benzylidene*-1 : 4-*benzopyranol*,  $\begin{array}{l}\mathrm{HO{\cdot}C{=}CH{-}{-}{-}C{\cdot}O{-}{-}{-}CPh} \\ \mathrm{CH{:}C(OH){\cdot}C{\cdot}C(CHPh){\cdot}CH}\end{array}$, is obtained from phenylacetylacetophenone and phloroglucinol; it forms orange-red crystals which sinter at 175°, melt and decompose at 241° and contain $1H_2O$; when boiled with concentrated aqueous potassium hydroxide, it is decomposed into acetophenone, dihydroxyphenyl benzyl ketone (?), and benzoic and phenylacetic acids.

The *picrate* crystallises in orange-red needles decomposing at 205°; the *diacetyl* derivative crystallises in yellowish-white needles which decompose at 148—149·5°; the *dimethoxy*-derivative is prepared by addition of methyl sulphate to an alkaline solution of the benzopyranol; it crystallises in yellow needles melting and decomposing at 140—142°.

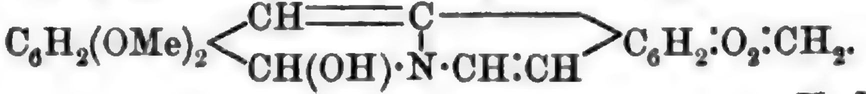
The *hydrochloride* of 6 : 7-*dihydroxy-2-phenyl-4-benzylidene*-1 : 4-*benzopyranol*,  $\begin{array}{l}\mathrm{OH{\cdot}C{:}CH{\cdot}C{-}{-}O{-}{-}CPh} \\ \mathrm{OH{\cdot}C{:}CH{\cdot}C{\cdot}C(CHPh){\cdot}CH}\end{array}$, is prepared from hydroxyquinol and phenylacetylacetophenone, and crystallises in small, brown leaflets, with $1\frac{1}{2}H_2O$, melting and decomposing at 169°. The benzopyranol is obtained from the hydrochloride by the addition of aqueous sodium acetate to its alcoholic solution; it forms ruby-red crystals decomposing at about 170° and shows a faint green fluorescence when dissolved in sulphuric acid. The *sulphate* crystallises in reddish-brown needles with $3H_2O$, begins to melt at 150°, and is completely liquefied at 183°; the *platinichloride* is a yellowish-brown, crystalline precipitate; the *picrate* forms brownish-red crystals melting and decomposing at 198°; the *diacetyl* derivative crystallises in lemon-yellow leaflets or needles and dissolves in sulphuric acid with a green fluorescence.

The *hydrochloride* of 7- (or 5-)*hydroxy-2-phenyl-4-benzylidene*-5- (or 7-) *methyl*-1 : 4-*benzopyranol* is prepared from phenylacetylacetophenone and orcinol, and crystallises with $4H_2O$ in orange-red needles; the *base* was only obtained as a brown precipitate which gave a yellow, fluorescent solution in sulphuric acid; the *picrate* forms crystals decomposing at 181°; the *cobalticyanide* crystallises in lustrous, red leaflets, which lose their colour at 190° and decompose at 200°. The *acetyl* derivative, prepared by treating the hydrochloride with acetic anhydride and pyridine, crystallises in yellow needles melting at 134°; the *benzoyl* derivative forms yellow needles decomposing at 134—136°; the *methoxy*-derivative, yellow leaflets melting at 141—145°.

K. J. P. O.

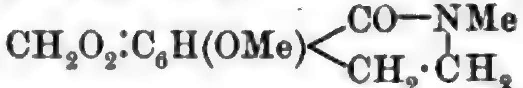
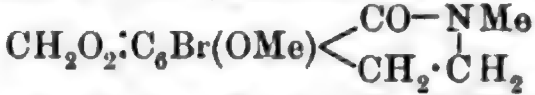
Constitution of Berberine. By JOHANNES GADAMER (*Chem. Zeit.*, 1902, **26**, 291—292; 385. Compare this vol., i, 273).—The formula for berberine (*loc. cit.*), which represents the alkaloid as a quaternary base, is confirmed by later observations. On treating a solution of acid berberine sulphate with barium hydroxide, a brownish-red, strongly alkaline solution of the free base, *berberinium hydroxide*, $C_{20}H_{19}O_5N$, is obtained; with excess of sodium hydroxide, this solution yields *berberinaldehyde,*  $\mathrm{CHO{\cdot}C_8H_8O_2{\cdot}CH{:}\begin{array}{l}C\text{———}\\ NH{\cdot}CH{:}CH\end{array}{>}C_6H_2{:}O_2{:}CH_2}$, which melts at 144°, and on warming with water is reconverted into berberinium hydroxide. By the action of concentrated sodium hydroxide, berberinaldehyde (2 mols.) yields *dihydroberberine*, $C_{20}H_{21}O_5N$ (1 mol.), and oxyberberine, $C_{20}H_{19}O_6N$ (1 mol.). Dihydroberberine is a yellow, crystalline base melting at 163—164°, and is the primary alcohol corresponding with the aldehyde berberinal, whilst oxyberberine (m. p. 198—199°) is the corresponding carboxylic acid. Dihydroberberine is converted into berberine when exposed to the air.

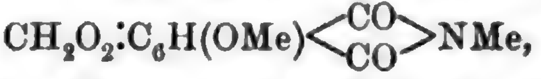
The second paper states that Roser has suggested that berberinal (*loc. cit.*) may not be an aldehyde, but the pseudoammonium hydroxide of berberine, and, in consequence, be represented by the formula

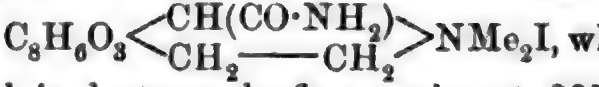
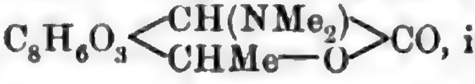


$$\mathrm{C_6H_2(OMe)_2{<}\begin{array}{l}CH{=\!=}C\text{———}\\ CH(OH){\cdot}N{\cdot}CH{:}CH\end{array}{>}C_6H_2{:}O_2{:}CH_2.}$$

K. J. P. O.

Cotarnine. By Martin Freund and Georg Wulff (*Ber.*, 1902, **35**, 1737—1739).—*Oxycotarnine,*  $\mathrm{CH_2O_2{:}C_6H(OMe){<}\begin{array}{l}CO{-}NMe\\ CH_2{\cdot}CH_2\end{array}}$, the principal product of the oxidation of cotarnine with aqueous potassium permanganate, crystallises from dilute alcohol in colourless prisms, with $1H_2O$, melting at 69—70°; when dry, it melts at 108°. The *platinichloride* melts and decomposes at 179—180°, and the *aurichloride* melts at 160°. *Bromo-oxycotarnine,*  $\mathrm{CH_2O_2{:}C_6Br(OMe){<}\begin{array}{l}CO{-}NMe\\ CH_2{\cdot}CH_2\end{array}}$, obtained by brominating the oxidation product, melts at 125—126°.

Cotarnic acid methylimide,  $\mathrm{CH_2O_2{:}C_6H(OMe){<}\begin{array}{l}CO\\ CO\end{array}{>}NMe}$, is also formed in small quantity along with cotarnic acid in the foregoing oxidation; it melts at 205—206°. W. A. D.

Cotarnine. By Martin Freund and Paul Bamberg (*Ber.*, 1902, **35**, 1739—1754).—Cyanohydrocotarnine methiodide (Freund, 1900, i, 248) is converted by warming with very dilute alkali into *hydrocotarnine carboxylamide methiodide,*  $\mathrm{C_8H_6O_3{<}\begin{array}{l}CH(CO{\cdot}NH_2)\\ CH_2\text{——}CH_2\end{array}{>}NMe_2I}$, which crystallises from dilute alcohol in lustrous leaflets, melts at 235°, and on boiling with concentrated potassium hydroxide, gives, by loss of hydrogen iodide, the *base* $\mathrm{CH_2{:}CH{\cdot}C_8H_6O_3{\cdot}CH(CO{\cdot}NH_2){\cdot}NMe_2}$; this crystallises from dilute alcohol in aggregates of needles, melts at 182°, and forms a crystalline *hydrochloride*, melting, when dry, at 207—208°, a *hydriodide* melting at 184°, and a *methiodide* melting at 195°. The *lactone,*  $\mathrm{C_8H_6O_3{<}\begin{array}{l}CH(NMe_2)\\ CHMe{-}O\end{array}{>}CO}$, is obtained by heating the base for 5—10 minutes with aqueous alcoholic hydrogen chloride, and separates from water in white crystals melting at 168°; it is converted by warm aqueous alkali into the *hydroxy-acid*,

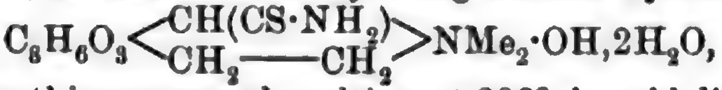
$$\mathrm{OH{\cdot}CHMe{\cdot}C_8H_6O_3{\cdot}CH(NMe_2){\cdot}CO_2H,}$$

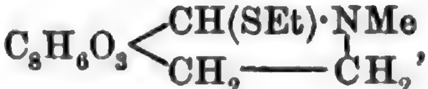
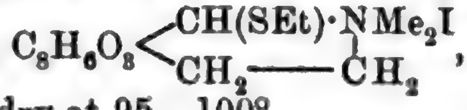
which melts at 207° and has both acid and basic properties.

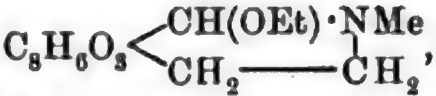
If, in hydrolysing the base, absolute alcoholic hydrogen chloride is employed under pressure at 100°, carbon dioxide is split off and the *compound*, $CH_2\!:\!CH\cdot C_8H_6O_3\cdot CH_2\cdot NMe_2$, formed; it crystallises from water and melts at 229—230°.

Hydrocotarninethiocarbonamide methiodide,

$$C_8H_6O_3<\begin{matrix}CH(CS\cdot NH_2)\\ CH_2\text{——}CH_2\end{matrix}>NMe_2I,$$

obtained by heating cyanocotarnine methiodide for a few minutes with ammonium sulphide, crystallises from water in short, thick, lemon-yellow prisms or long, lustrous needles, melts at 203°, and when boiled with potassium hydroxide solution is converted by loss of hydrogen iodide and hydrogen sulphide into the foregoing base melting at 182°. With dilute aqueous sodium hydrosulphide, on the other hand, cyanocotarnine methiodide gives the same compound, melting at 235°, as was obtained by using sodium hydroxide. The *ammonium base*,  $C_8H_6O_3<\begin{matrix}CH(CS\cdot NH_2)\\ CH_2\text{——}CH_2\end{matrix}>NMe_2\cdot OH,2H_2O$, obtained by suspending the thio-compound, melting at 203°, in cold dilute sodium hydroxide, crystallises in nacreous leaflets and melts at 135° when hydrated, at 141—142° when anhydrous.

Ethylmercaptohydrocotarnine,  $C_8H_6O_3<\begin{matrix}CH(SEt)\cdot NMe\\ CH_2\text{——}CH_2\end{matrix}$, obtained by adding ethyl mercaptan to cotarnine suspended in ether, separates from the latter in well-formed crystals and melts at 55°; the *methiodide*,  $C_8H_6O_3<\begin{matrix}CH(SEt)\cdot NMe_2I\\ CH_2\text{——}CH_2\end{matrix}$, with $1H_2O$, melts at 75—80°, or when dry at 95—100°

Ethoxyhydrocotarnine,  $C_8H_6O_3<\begin{matrix}CH(OEt)\cdot NMe\\ CH_2\text{——}CH_2\end{matrix}$, is obtained by evaporating an absolute alcoholic solution of cotarnine in a vacuum.

For a justification of the preceding formulæ, the original should be consulted.

W. A. D.

The Existence of Lysatinine. By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1902, **35**, 192—195. Compare Hedin, *ibid.*, 1895, **21**, 297).—Experiments are described which tend to show that the silver derivative of lysatinine is not a mixture of the silver derivatives of lysine and arginine in molecular proportions as suggested by Hedin.

J. J. S.

Lupinine. By RICHARD WILLSTÄTTER and ERNEST FOURNEAU (*Ber.*, 1902, **35**, 1910—1926).—The low boiling point of lupinine and its derivatives points to a simpler formula than $C_{21}H_{40}O_2N_2$ (Baumert, Abstr., 1881, 831; 1882, 229, 873); the analytical data were found to agree equally well with the formula $C_{10}H_{19}ON$, and this was confirmed by cryoscopic measurements of lupinine and benzoyl-lupinine. Lupinine is a tertiary base, contains no methyl groups attached to nitrogen, is saturated, and therefore contains two ring systems, and is not altered by sodium amyloxide in amyl alcohol under conditions which convert tropine into ψ-tropine. With phenylcarbimide, it forms the *compound*

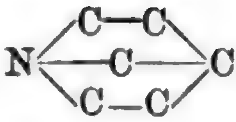
$(C_{10}H_{18}N)O·CO·NHPh$, which crystallises from absolute alcohol in glistening prisms and needles, is insoluble in water, and melts at 94—95°; lupinine therefore contains a hydroxyl group.

Anhydrolupinine, $C_{10}H_{17}N$, prepared by heating lupinine with acetic and sulphuric acids at 180°, is a colourless oil of unpleasant, narcotic odour, boils at 216·5—217·5° under 726 mm. pressure, is oxidised by potassium permanganate, and apparently by picric acid. The *platinichloride*, $(C_{10}H_{17}N)_2,H_2PtCl_6$, separates from water in reddish-brown crystals, which are stable in air, darkens at 170°, and decomposes at 216°. The *aurichloride*, $C_{10}H_{17}N,HAuCl_4$, forms transparent, golden-yellow prisms and, when quickly heated, melts at 140—141°. The *methiodide*, $C_{10}H_{17}N,MeI$, forms sharp-edged flakes and decomposes and melts at 180°.

Lupinic acid, $C_9H_{16}N·CO_2H$, prepared by oxidising lupinine with chromic acid, crystallises from dilute acetone in splendid, long, colourless needles containing $3H_2O$. The anhydrous acid, when quickly heated, melts without darkening and without decomposing at 255°, and can be sublimed in a test-tube; it is readily soluble in water or alcohol, but not in dry acetone or ether, does not reduce silver oxide or permanganate, and does not form metallic salts, but gives salts with acids; the *hydrochloride*, $C_{10}H_{17}O_2N,HCl$, separates from alcohol in stout, well-developed, prismatic crystals, is very easily soluble in water, and melts and decomposes at 275°; the *platinichloride*, $(C_{10}H_{17}O_2N)_2,H_2PtCl_6,3H_2O$, is readily soluble in water, but crystallises from moist acetone or ether in short, transparent, red prisms, darkens at 120°, and decomposes vigorously at 235°; the *aurichloride*, $C_{10}H_{17}O_2N,HAuCl_4$, is only slightly soluble in cold water, crystallises in long, golden-yellow needles, and melts at 188°. The *methyl* ester, $C_9H_{16}N·CO_2Me$, is a colourless, mobile oil, boils at 131° under 15 mm. pressure, has a strong alkaline reaction, is little soluble in cold, and less so in hot, water; the aurichloride was obtained as an oil; the *platinichloride*, $(C_{11}H_{19}O_2N)_2,H_2PtCl_6$, crystallises from hot water in orange-coloured needles, and melts and decomposes at 210—212°; the *methiodide*, $C_{11}H_{19}O_2N,MeI$, forms glistening, white tablets, melts with slight evolution of gas at 225—226°, and is stable towards alkalis, indicating that it is probably derived from a β-amino-acid.

Methyl-lupuline, $C_{10}H_{18}ONMe$, prepared by distilling lupulinemethylammonium hydroxide under reduced pressure, is a colourless, viscid oil of slight fishy odour, boils at 145—146° under 15 mm. pressure, is soluble in about 50 parts of cold, less so in hot, water, is not very readily volatile with steam, behaves as a tertiary base, reduces potassium permanganate, gives an oily aurichloride and a syrupy platinichloride, and may perhaps contain two isomeric compounds. The *methiodide*, $C_{10}H_{18}ONMe_2I$, crystallises from alcohol in long, colourless prisms and melts at 224—225°, but the product is not homogeneous, and more than half of it remains as a syrup.

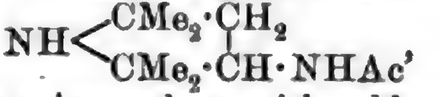
Dimethyl-lupuline, $C_{10}H_{17}ONMe_2$, boils at 169—172° under 28—29 mm. pressure, and resembles methyl-lupuline. When the ammonium hydroxide of this base is distilled, it loses the whole of the nitrogen as trimethylamine, leaving a compound which behaves as an unsaturated alcohol.

Lupinine probably contains a ring system,  $\mathrm{N}{<}\begin{matrix}\mathrm{C{-}C}\\ \mathrm{C}\\ \mathrm{C{-}C}\end{matrix}{>}\mathrm{C}$, similar to that which exists in cinchonine. T. M. L.

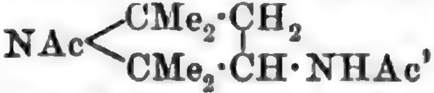
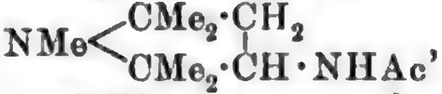
Conversion of Tropidine into Tropine. By RICHARD WILLSTÄTTER (*Ber.*, 1901, **35**, 1870).—Ladenburg's method for the conversion of tropidine into tropine (this vol., i, 390) depends on the action of dilute acid at 160° on a mixture of α- and β-bromotropans, and therefore closely resembles that previously employed by the author (Abstr., 1901, i, 744). A. H.

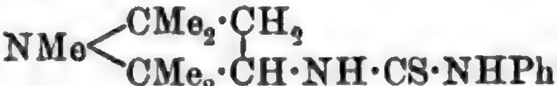
The Hydropyrrole Series. By HERMANN PAULY (*Annalen*, 1902, **322**, 77—130. Compare Abstr., 1899, i, 773, 872; 1900, i, 357; 1901, i, 607).—3-Amino-2 : 2 : 5 : 5-tetramethylpyrrolidine yields the following derivatives: the *platinichloride*, $C_8H_{18}N_2,H_2PtCl_6,3H_2O$, crystallising in orange-red, twinned prisms, becoming anhydrous at 105°, and decomposing at 215°; the *picrate*, $C_8H_{18}N_4,2C_6H_2(NO_2)_3OH$, forming yellow needles melting at 242°, and the *carbamate*, $C_9H_{18}O_2N_2$, separating from ether in white, microscopic needles and sintering and decomposing at 142—145°.

3-*Acetylamino*-2 : 2 : 5 : 5-*tetramethylpyrrolidine*,



$$\mathrm{NH}{<}\begin{matrix}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CH\cdot NHAc}\end{matrix}$$

produced on mixing the primary base with cold acetic anhydride, boils at 150—151° under 13—14 mm., and at 155° under 16 mm. pressure; it solidifies in spherical aggregates melting at 70°; its hydrochloride is readily soluble in water and yields a nitrosoamine with nitrous acid; the *aurichloride* dissolves but sparingly in the cold solvent and crystallises in rhombic plates decomposing at 213°. The *diacetyl* compound,  $\mathrm{NAc}{<}\begin{matrix}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CH\cdot NHAc}\end{matrix}$, obtained by the further action of acetic anhydride, separates from benzene in small, well-defined crystals and melts at 166—167°. 2 : 2 : 5 : 5-Tetramethyl-Δ³-pyrroline forms a soluble hydrochloride and hydriodide; the *picrate* crystallises from alcohol in spherical aggregates of needles melting at 255—256° when rapidly heated and decomposing at 240° when slowly heated. The *aurichloride* separates from aqueous solutions of its generators as an oil solidifying in yellow needles; the *platinichloride*, $(C_8H_{15}N)_2,H_2PtCl_6,2H_2O$, crystallises from water in oblique, tabular prisms; it becomes anhydrous at 100° and decomposes at 200°. 3-Amino-1 : 2 : 2 : 5 : 5-pentamethylpyrrolidine furnishes a *picrate*, $C_9H_{20}N_2,2C_6H_2(NO_2)_3\cdot OH$, crystallising in yellow needles from an alcoholic solution of its generators and melting at 215°; the normal *oxalate*, $C_9H_{20}N_2,H_2C_2O_4$, separates, on adding dry oxalic acid to an ethereal solution of the amine, in small, triangular or hexagonal plates melting at 216°. 3-*Acetylamino*-1 : 2 : 2 : 5 : 5-*pentamethylpyrrolidine*,  $\mathrm{NMe}{<}\begin{matrix}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CMe_2\cdot CH\cdot NHAc}\end{matrix}$, boils at 145—146° under 11 mm. pressure and solidifies to a mass of radiating crystals melting at 87°.

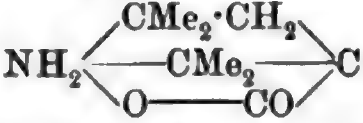
The *phenylthiocarbamide*, , produced by mixing the diamine with phenylthiocarbimide in methyl alcohol, crystallises from this solvent in silky needles and melts at 146°; its hydrochloride is readily soluble and yields a sparingly soluble aurichloride and platinichloride.

The *a*-thiocarbamate of 3-amino-2 : 2 : 5 : 5-pyrrolidine is readily transformed into its *b*-isomeride on boiling with water for a short time (Abstr., 1901, i, 607). This transformation does not readily occur in the case of the *a*-thiocarbamate of 3-amino-1 : 2 : 2 : 5 : 5-pentamethylpyrrolidine; this substance, which, when freshly prepared, melts at 103°, becomes altered after two days and then sinters at 46°, effervesces at 90°, and completely decomposes at 125°.

3-Keto-2 : 2 : 5 : 5-tetramethylpyrrolidine (compare Pauly and Boehm, Abstr., 1901, i, 607) forms a soluble *hydrochloride*, $C_8H_{15}ON,HCl$, and *hydriodide* crystallising in needles; the *aurichloride*, $C_8H_{15}ON,HAuCl_4$, separates in light yellow needles and melts at 178°, the *platinichloride* forms orange-coloured, quadratic plates, and the *picrate*,

$$C_8H_{15}ON,C_6H_2(NO_2)_3\cdot OH,$$

crystallises from alcohol in yellow leaflets and melts at 226°.

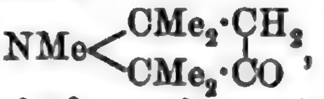
The *hydrochloride*, , of the amino-acid, obtained by hydrolysing the cyanohydrin of the keto-base with concentrated hydrochloric acid at −10°, crystallises from water in prisms or hexagonal plates, evolving water at 120° and melting at 226°; both the hydrochloride and the free acid are readily soluble in water.

3-Hydroxy-2 : 2 : 5 : 5-tetramethylpyrrolidine, obtained by reducing the keto-base with sodium amalgam, yields a *hydrochloride* crystallising in needles readily soluble in water or alcohol, but dissolving very sparingly in boiling acetone. The base,

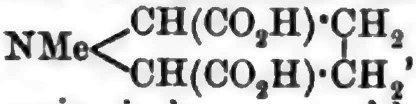
$$C_8H_{19}ON\ [=NH_2\cdot CMe_2\cdot CH_2\cdot CH(OH)\cdot CHMe_2\ ?],$$

also formed in this reduction and separated from the other product by means of the ready solubility of its hydrochloride in acetone, furnishes a *platinichloride*, $C_8H_{19}ON,H_2PtCl_6$, crystallising in orange-coloured, rhombic plates containing 1 mol. of alcohol of crystallisation and melting at 170°. This base, when treated with nitrous acid, yields a yellow oil resembling the ethereal nitrites; on oxidation, it gives rise to ammonia and a product boiling at 150° and having an odour resembling that of mesityl oxide.

3-*Hydroxy*-2 : 2 : 5 : 5-*tetramethylpyrrolidine mandelate* is a white, resinous product having a powerful mydriatic action.

3-*Keto*-1 : 2 : 2 : 5 : 5-*pentamethylpyrrolidine*, , prepared by treating 1 : 2 : 2 : 5 : 5-pentamethyl-Δ^3-pyrrolinecarboxylamide with potassium hypobromite, boils at 187—188° under 755 mm. pressure and solidifies to a mass of feathery crystals melting at 43°; the substance has the odour both of ammonia and camphor, and on exposure to the air assumes a reddish-brown colour. The *hydriodide* crystallises in long needles melting above 220°; the platinichloride and hydrochloride are both very soluble salts; the *oxime* sublimes in needles soluble in water, alcohol, or ether, and melts at 104°.

A considerable portion of the experimental part of this communication has already been published; the theoretical part includes a discussion of the genetic relationships of the hydropyrrole derivatives, the connection between the different members of the series being also illustrated by means of a diagram. G. T. M.

***N*-Methylpyrrolidine-α_1-α_2-dicarboxylic Acid [1-Methylpyrrolidine-2 : 5-dicarboxylic Acid].** By RICHARD WILLSTÄTTER and RUDOLF LESSING (*Ber.*, 1902, 35, 2065—2073. Compare Abstr., 1899, i, 633; 1900, i, 405; 1901, i, 650; and this vol., i, 266).—*Ethyl αδ-dibromoadipate*, $C_4H_6Br_2(CO_2Et)_2$, prepared from the corresponding acid, crystallises in colourless prisms or needles melting at 65·5—66·5°, and is converted into 1-*methylpyrrolidine*-2 : 5-*dicarboxylic acid*,  $NMe\genfrac{}{}{0pt}{}{\diagup CH(CO_2H)\cdot CH_2}{\diagdown CH(CO_2H)\cdot CH_2}$, by heating with a dry solution of methylamine in benzene and hydrolysing the ester thus formed with barium hydroxide; the acid crystallises in six-sided prisms and changes colour at 235° and finally melts and decomposes at 273—274°; it resembles tropic acid closely, but is less soluble in water; it is not oxidised by acid permanganate, but readily by alkaline permanganate and silver oxide. Its vapour colours a pine splinter moistened with hydrochloric acid intensely red. Measurements of the electrical conductivity show that even at high concentrations it behaves as a dibasic acid, whereas tropic acid behaves as a monobasic acid and has κ 0·0426. The *copper* salt, $C_7H_{10}O_4NCu\cdot OH,5H_2O$, crystallises in pale blue leaflets; when dried at 105°, $1H_2O$ is still retained; it melts and decomposes at 240°. The *silver* salt crystallises in slender needles. The *hydrochloride* forms six-sided prisms or plates which become coloured at 235°, decompose at 261—262° and are hydrolysed by water; the *platinichloride* forms six-sided prisms. *Methyl* 1-*methylpyrrolidine*-2 : 5-*dicarboxylate* crystallises in long needles, melts at 35—36°, and boils at 140° under 17—18 mm. pressure; the *methiodide* of the ester crystallises in prisms decomposing at 120—120·5°.

1-*Methylpyrrolidine* 2 : 3 : 4 : 5-*tetracarboxymethylamide*,

$$C_4H_4NMe(CO\cdot NHMe)_4,$$

is obtained by heating an alcoholic solution of ethyl αδ-dibromobutanetetracarboxylate and methylamine for 10 hours; it forms colourless, four-sided prisms melting at 230—230·5°. On hydrolysis with barium hydroxide, a methylpyrrolidinedicarboxylic acid is formed which melts at 280—281° and is far less soluble than its isomeride.

Methyl 1-*methylpiperidine*-2 : 6-*dicarboxylate* is prepared by heating ethyl dibromopentanetetracarboxylate (b. p. 251—253° under 12 mm. pressure) with a benzene solution of methylamine under pressure at 140—150°; the product is boiled with concentrated barium hydroxide, and the dicarboxylic acid thus obtained converted into its methyl ester; this ester is a colourless oil boiling at 140—141° under 13 mm. pressure. The *methiodide* crystallises in monoclinic prisms melting at 167—168°. K. J. P. O.

Phenolic Urethanes of Piperidine. By BOUCHETAL DE LA ROCHE (*Bull. Soc. Chim.*, 1902, [iii], **27**, 451—453).—Employing Cazeneuve and Moreau's method (Abstr., 1899, i, 132), the author has prepared the following urethanes of piperidine. o-*Chlorophenyl piperidinecarbamate*, $C_5H_{10}N\cdot CO\cdot O\cdot C_6H_4Cl$, crystallises in colourless octahedra melting at 119° and boiling at 148—149° under 273 mm. pressure; it is insoluble in water but soluble in alcohol. p-*Chlorophenyl piperidinecarbamate* is a yellow, crystalline substance which melts at 65° and boils at 218—219° under 23 mm., and at 284—285° under atmospheric pressure, at the same time rapidly undergoing decomposition; it is soluble in water, ether, carbon disulphide, acetone, or chloroform, and very soluble in hot alcohol. *Pentachlorophenyl piperidinecarbamate* forms lustrous, white crystals, melts at 123°, and boils at 259° under 11 mm. pressure; it is sparingly soluble in hot alcohol but fairly so in benzene. o-*Tolyl piperidinecarbamate* crystallises in white prisms and is very soluble in organic solvents; it melts at 32° and boils at 193° under 17 mm. pressure, and with decomposition at 310° under atmospheric pressure. m-*Tolyl piperidinecarbamate* melts at 64°, boils at 195° under 10·7 mm. pressure, and is soluble in alcohol, chloroform, ether, or acetone. p-*Tolyl piperidinecarbamate* forms white needles melting at 85° and boiling at 201° under 15 mm. pressure and at 320° under atmospheric pressure, undergoing at the same time slight decomposition. *Eugenyl piperidinecarbamate* crystallises in white plates which melt at 93·5—94° and boil at 239° under 18 mm. pressure. *Thymyl piperidinecarbamate* has only been obtained as a yellow liquid boiling in a vacuum at 204—206°.

A. F.

Relations of Hydrogen to Unsaturated Elements and Groups of Elements. By DANIEL VORLÄNDER (*Ber.*, 1901, **35**, 1845—1846).—The reactions of certain pyrrole derivatives which appear to Feist (this vol., i, 490) to be anomalous fall within the scope of the author's theory (Abstr., 1901, i, 444) and must therefore be considered normal.

A. H.

Furfuran and Pyrrole Groups. By EDUARD A. KEHRER (*Ber.*, 1902, **35**, 2009—2010).—In reply to Feist (this vol., i, 488), the author points out that 1 : 4-diketones may be readily obtained by the methods previously described (Abstr., 1899, i, 568; 1901, i, 389), and that on treatment with ammonia these diketones give good yields of pyrrole derivatives.

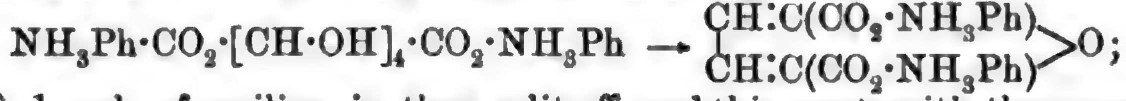
J. J. S.

Mechanism of the Formation of Pyrrole from the Salts of Mucic Acid. By AMÉ PICTET and ALBERT STEINMANN (*Arch. Sci. phys. nat.*, 1902, [iv], **13**, 342—351).—When normal aniline mucate is heated strongly, 1-phenylpyrrole is formed together with *s*-diphenylcarbamide. When heated at 240° for an hour, a residue is obtained from which 1-phenylpyrrole-2-carboxylic acid and 1-phenylpyrrole-2 : 5-dicarboxylic acid can be isolated.

1-*Phenylpyrrole-2-carboxylic acid* is obtained by dissolving the residue in alkali and precipitating with hydrogen chloride; when crystallised from alcohol or benzene, it forms white needles which are odourless and tasteless and melt at 166°; when fused, it decomposes into carbon dioxide and 1-phenylpyrrole. It is insoluble in cold water, and decomposed when boiled with water, but is easily soluble in alcohol, benzene, or chloroform, less so in acetic acid, sparingly in ether. Its alcoholic solution, to which hydrochloric acid has been added, imparts a violet coloration to a pine splinter immersed in it. The *ammonium*, *silver*, *copper*, and *calcium* salts have been prepared. The *methyl* ester boils at 282° without decomposition, forms colourless crystals which melt at 88°, and is very soluble in ether, benzene, chloroform, or acetic acid. The corresponding *ethyl* ester is a colourless liquid which boils at 289° and does not colour a pine splinter.

After extracting the monocarboxylic acid, crystals of 1-*phenylpyrrole-2 : 5-dicarboxylic acid* separate from the mother liquor. This substance has no definite melting point; at 240°, it decomposes into carbon dioxide and 1-phenylpyrrole; it is only sparingly soluble in cold water, chloroform, or benzene, but very easily in hot water, acetic acid, alcohol, or ether. It gives an insoluble silver salt.

On account of the formation of these two substances, the authors conclude that the formation of 1-phenylpyrrole from aniline mucate takes place in the following stages: (1) 3 mols. of water are eliminated and the corresponding dehydromucate is produced:



$$NH_3Ph\cdot CO_2\cdot[CH\cdot OH]_4\cdot CO_2\cdot NH_3Ph \rightarrow \left.\begin{array}{l} CH{:}C(CO_2\cdot NH_3Ph) \\ | \\ CH{:}C(CO_2\cdot NH_3Ph)\end{array}\right\rangle O;$$

(2) 1 mol. of aniline is then split off, and this reacts with the oxygen in the ring with elimination of another mol. of water and formation of the aniline hydrogen salt of 1-phenylpyrrole-2 : 5-dicarboxylic acid; (3) the third phase is the splitting off of carbon dioxide with production of the aniline salt of 1-phenylpyrrole-2-carboxylic acid. The 1-phenylpyrrole is produced finally by the elimination of a mol. of aniline and one of carbon dioxide from the last salt. J. McC.

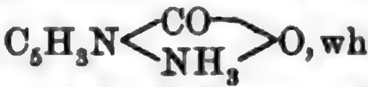
Compounds of Silver Chloride with Organic Bases. By Carl Renz (*Ber.*, 1902, **35**, 1954—1956).—Silver chloride dissolves in pyridine and in a solution of pyridine in hydrochloric acid, a double-salt being formed. This can be separated in crystalline form by evaporating the acid solution, and can be freed from pyridine hydrochloride by shaking with amyl alcohol. It has the formula $AgCl,2(C_5H_5N,HCl)$, is unchanged by light, and permanent at the ordinary temperature, is soluble without decomposition in acetone, is not decomposed by amyl alcohol or benzene, but liberates silver chloride in contact with water, alcohol, ether, methyl alcohol, or glycerol.

The quinoline double salt, $AgCl,C_9H_7N,HCl$, forms white needles, is permanent at the ordinary temperature, is not changed by light, and is decomposed by amyl alcohol as well as by water and alcohol, but can be purified by washing with ether. T. M. L.

Condensation of Quinaldine with Cuminaldehyde and *p*-Tolualdehyde. By Felix von Grabski (*Ber.*, 1902, **35**, 1956—1958). —*Quinaldyl*-p-*isopropyl-a-stilbazole*, $C_{20}H_{19}N$, prepared by heating quinaldine with cuminaldehyde at 180—190°, crystallises from alcohol in colourless, thread-like needles and melts at 102°. The *hydrochloride*, $C_{20}H_{19}N,HCl$, crystallises from dilute hydrochloric acid in small, yellow needles, sinters at 68°, and melts at 186°. The *platinichloride* forms yellow crystals and melts at 229—230°. The *mercurichloride* forms glistening, yellow needles and melts at 207—208°. The *picrate* forms dark yellow tablets and melts at 212°. The *dibromide*, $C_{20}H_{19}NBr_2$, crystallises from hot alcohol in colourless, glistening flakes and melts at 151°. The *stilbazoline*, prepared by reducing with sodium and alcohol, was obtained as a syrupy liquid; the *hydrochloride*, $C_{20}H_{25}N,HCl$, crystallises in colourless, feathery needles.

Quinaldyl-p-*methyl-a-stilbazole*, $C_{18}H_{15}N$, prepared in a similar manner from quinaldine and *p*-tolualdehyde, crystallises from alcohol in long, yellow needles. The *hydrochloride* forms slender, yellow needles, sinters at 115° and melts at 218°. The *platinichloride*, *mercurichloride*, and *picrate* were also prepared and analysed. *Quinaldyl*-p-*methyl-a-stilbazoline*, $C_{18}H_{21}N$, is a thick oil, and boils at 249—250° under 25 mm. pressure. The *hydrochloride* forms pale yellow needles, sinters at 220°, and melts at 229°.

Quinaldyl-a-stilbazoline, $C_{17}H_{19}N$, prepared by reducing Wallach and Wüsten's benzylidinequinaldine (Abstr., 1883, 1096), is a thick, yellowish oil, and boils at 229—230° under 20 mm. pressure. The *hydrochloride* forms white needles, darkens in colour when heated and melts at 210—211°. The *benzoyl* derivative forms slender, silky needles and melts at 107°. T. M. L.

Isomeric Change of Methyl Cinchomeronate into Apophyllenic Acid. By ALFRED KIRPAL (*Monatsh.*, 1902, **23**, 239—249. Compare Abstr., 1901, i, 227).—Cinchomeronic acid is converted by sodium hypobromite into 4-*aminonicotinic acid*,  $C_5H_3N\langle{}^{CO-}_{NH_3}\rangle O$, which crystallises from water in thick, colourless prisms or in delicate needles and decomposes at above 340°. The *sulphate*, $(C_6H_6O_2N_2)_2,H_2SO_4$, crystallises from dilute sulphuric acid in long, colourless needles, the *hydrochloride* forms delicate, glistening needles and decomposes at 270°, the *platinichloride* forms orange-coloured prisms and decomposes at 250°. When heated at 340°, the acid decomposes into carbon dioxide and 4-aminopyridine (m. p. 154°). When heated with methyl alcohol and hydrogen chloride, the acid forms its *methyl* ester which is easily soluble in hot chloroform or alcohol, melts at 173°, and is easily hydrolysed by alkalis or concentrated sulphuric acid, but with great difficulty by the dilute acid. 4-Aminonicotinic acid cannot be diazotised in dilute sulphuric acid solution; when diazotised in concentrated sulphuric acid and boiled, after addition of water, it is converted into 4-*hydroxynicotinic acid* which melts with evolution of gas at 250° and yields 4-hydroxypyridine (m. p. 66°).

When γ-methyl cinchomeronate is heated at 154°, it is converted into apophyllenic acid, which crystallises from water in needles and melts at 240°. Apophyllenic acid must be *iso*nicotinic-betaine-3-carboxylic acid (compare Abstr., 1886, 369). G. Y.

Cinchomeronic Acid and Apophyllenic Acid. By KARL KAASS (*Monatsh.*, 1902, **23**, 250—261).—Cinchomeronic acid is best purified by recrystallisation of its hydrochloride. α-Methyl cinchomeronate, prepared by treatment of the anhydride with methyl alcohol, yields a violet, crystalline, copper salt (compare Abstr., 1900, i, 51). *β-Methyl cinchomeronate* is formed by hydrolysis of dimethyl cinchomeronate with cold alcoholic potassium hydroxide; it is a crystalline powder, soluble in methyl alcohol, melts at 160°, and yields a light blue, crystalline, copper salt which does not change its colour on warming.

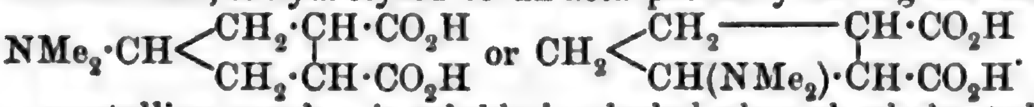
When heated with methyl iodide at 100°, α-methyl cinchomeronate yields apophyllenic acid and a *methiodide*, $CO_2H\cdot C_5NH_3\cdot CO_2Me,MeI$, which forms granular crystals and melts at 223—224°. β-Methyl cinchomeronate forms a *methiodide* which melts at 188°, but not apophyllenic acid.

When heated at 180°, α-methyl cinchomeronate yields cinchomeronic acid and apophyllenic acid.

Apophyllenic acid prepared from α-methyl cinchomeronate or from cotarnine melts at 229—232° (compare Kirpal, preceding abstract).

Note.—The ester termed α-methyl by this author is the γ-methyl ester of Kirpal. G. Y.

Hofmann's Reaction. By ZDENKO H. SKRAUP and G. PICCOLI (*Monatsh.*, 1902, 23, 269—285. Compare Abstr., 1901, i, 226).—Diethyl methylhexahydrocinchomeronate is a light yellow liquid, has a slight amine-like odour, boils at 153—155° under 26 mm. pressure and yields, with methyl iodide, a *methiodide* which crystallises in microscopic, triangular plates, is soluble in cold water or boiling alcohol, and melts at 141°. When treated with potassium hydroxide in concentrated aqueous solution, the methiodide yields an oil, which, when boiled with dilute alkali, is hydrolysed to an *acid* probably having the constitution



$\mathrm{NMe_2\cdot CH}<\begin{matrix}\mathrm{CH_2\cdot CH\cdot CO_2H}\\ \mathrm{CH_2\cdot CH\cdot CO_2H}\end{matrix}$ or $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2 \text{———} CH\cdot CO_2H}\\ \mathrm{CH(NMe_2)\cdot CH\cdot CO_2H}\end{matrix}$. It forms a crystalline powder, is soluble in alcohol when slowly heated, becomes brown at 245°, and melts and decomposes at 263°. If introduced into a bath at 230° and rapidly heated, it melts at 273°. The *potassium* and *copper* salts are described. The *platinichloride* crystallises in long plates, sinters at 235°, and melts at 239°. The *aurichloride* melts at 195°. When fused with potassium hydroxide, diethyl methylhexahydrocinchomeronate methiodide yields α-methyltricarballylic acid (Abstr., 1892, 41) and small quantities of oxalic acid. G. Y.

Isomeric Dihydrolutidinedicarboxylic Esters of R. Schiff and P. Prosio. By EMIL KNOEVENAGEL and J. FUCHS (*Ber.*, 1902, 35, 1788—1799).—Schiff and Prosio (Abstr., 1896, i, 250) stated that ethyl dihydrolutidinedicarboxylate (m. p. 183—185°) was converted by concentrated hydrochloric acid into an isomeric ester melting at 58—62°. It is shown by the authors that this product is a mixture of ethyl lutidinedicarboxylate (2 mols.) and ethyl hexahydrolutidinedicarboxylate (1 mol.). From this mixture, the former ester can be separated in the form of the picrate. By the action of sodium nitrite on the mixture, the yellow *nitroso*-derivative of ethyl hexahydrolutidinedicarboxylate, $C_{13}H_{22}O_5N_2$, is obtained, melting at 54°; on reduction, it yields ammonia and the original hexahydro-ester. By means of light petroleum, the mixture (m. p. 58—62°) can be separated into ethyl lutidinedicarboxylate (m. p. 73°) which is readily soluble, and ethyl hexahydrolutidinedicarboxylate (m. p. 92—94°), which is insoluble. The last-mentioned substance crystallises in small, white cubes and is very readily oxidised by the air (taking up 2 atoms of oxygen and losing 1 mol. of water). The *platinichloride* melts and decomposes at 128°. The *platinichloride* of ethyl lutidinedicarboxylate forms golden yellow crystals melting at 197°. K. J. P. O.

Formation of Dinitrophenoxazines. By J. C. Crocker (*Proc. Camb. Phil. Soc.*, 1902, 11, 342—346).—The products of reaction of picryl chloride on some *o*-hydroxyamino-compounds have been examined.

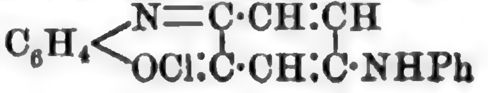
In alcoholic solution, sodium amino-β-naphtholsulphonate gives, with picryl chloride, bronze crystals of sodium naphthadinitrophenoxazinesulphonate. *o*-Aminophenolsulphonic acid gives a rouge-coloured powder of sodium dinitrophenoxazinesulphonate, which is almost insoluble in alcohol or acetic acid. α-Amino-β-naphthol gives brown, silky needles of naphthadinitrophenoxazine which decompose at 274°. *o-p*-Diaminophenol gives dipicraminophenol in the form of dark-red plates which melt at 185°, are easily soluble in acetic acid or cold potassium hydroxide solution, but only sparingly so in alcohol. Dipicraminophenol gives, with acetyl chloride, dipicraminophenyl acetate, which separates from dilute acetic acid in reddish-yellow plates melting at 223°. Dipicraminophenol is extremely soluble in aniline, and from the solution alcohol precipitates brown crystals which contain aniline and melt at 269°. After evaporation of the aniline and crystallisation from dilute acetic acid, a dark bronze powder of picraminodinitrophenoxazine is obtained melting at 277°. The aminophenol may also be condensed with sodium phosphate to form oxazine.

Aminothymol [$CH_3 : NH_2 : Pr : OH = 1 : 2 : 4 : 5$] gives, with picryl chloride, a brownish powder of picraminothymol which melts at 212°. J. McC.

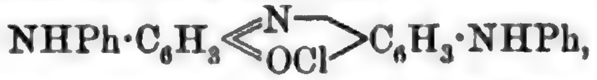
Constitution of the Oxazine and Thiazine Colouring Matters and their Relationship to the Azonium Compounds. By Friedrich Kehrmann (*Annalen*, 1902, 322, 1—77. Compare Abstr., 1900, i, 62; 1901, i, 484; this vol., i, 186, 235, and Green, Abstr., 1900, i, 119).—In the light of recent investigations, oxazine and thiazine colouring matters must be regarded, not as *p*-quinone derivatives but as compounds of the *o*-quinone type; the parent substances of the two series having the formulæ $C_6H_4{<}\genfrac{}{}{0pt}{}{N-}{OX}{>}C_6H_4$ and

$$C_6H_4{<}\genfrac{}{}{0pt}{}{N-}{SX}{>}C_6H_4,$$

analogous with the azonium salts, $C_6H_4{<}\genfrac{}{}{0pt}{}{N-\!-\!-}{NPhX}{>}C_6H_4$, where X is an acid radicle.

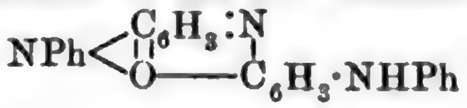
[With Carlo Stampa.]—Although phenazoxone, obtained by oxidising phenoxazine is unstable, yet the products formed by carrying out this operation in the presence of amines are readily isolated. *3-Anilinophenazoxonium chloride*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{N{=}C\cdot CH{:}CH}{OCl{:}C\cdot CH{:}C\cdot NHPh}$, produced in this way by the action of an alcoholic solution of ferric chloride and aniline hydrochloride, crystallises from this solvent in deep red, transparent leaflets and melts at 196—198°; the corresponding *nitrate* crystallises from hot water in dark red needles having a brass-like lustre.

3 : 9-*Dianilinophenazoxonium chloride*,



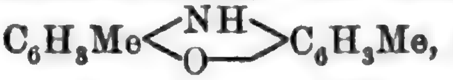
$$\mathrm{NHPh{\cdot}C_6H_3}<\!\!\begin{matrix}\mathrm{N}\\ \mathrm{OCl}\end{matrix}\!\!>\mathrm{C_6H_3{\cdot}NHPh},$$

prepared by treating the preceding salt with aniline hydrochloride and aniline, separates from dilute alcohol in lustrous spangles with a golden reflex. On rendering the solution of this salt alkaline with sodium carbonate, the anhydro-base,



$\mathrm{NPh}<\!\!\begin{matrix}\mathrm{C_6H_3{:}N}\\ \mathrm{O{-\!-\!-}C_6H_3{\cdot}NHPh}\end{matrix}$, is obtained as a green, crystalline powder.

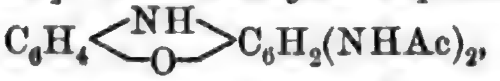
A mixture of dimethylphenoxazines is produced by condensing 2-methylcatechol with 4-amino-*m*-cresol, one isomeride, probably 3 : 9-dimethylphenoxazine,



$\mathrm{C_6H_3Me}<\!\!\begin{matrix}\mathrm{NH}\\ \mathrm{O}\end{matrix}\!\!>\mathrm{C_6H_3Me}$, crystallises from benzene in light grey plates melting at 204—205°; the other base has not yet been obtained pure. The former isomeride readily yields azoxonium salts on oxidation; *dimethylphenazoxonium picrate* is a violet, crystalline powder.

[With Walter Urech.]—3-*Methylphenoxazine*, prepared from catechol and 4-amino-*m*-cresol, separates from light petroleum in colourless, granular crystals melting at 123—125°, and yields only a monanilino-oxonium compound on treatment with aniline and an oxidising agent.

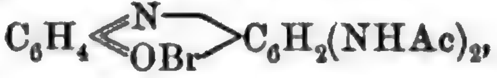
[With Paul Thomas.]—3 : 5-*Diacetylaminophenoxazine*,



$$\mathrm{C_6H_4}<\!\!\begin{matrix}\mathrm{NH}\\ \mathrm{O}\end{matrix}\!\!>\mathrm{C_6H_2(NHAc)_2},$$

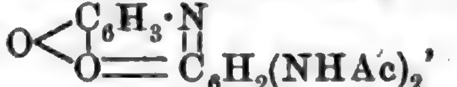
produced by warming the stannochloride of diaminophenoxazine (compare Abstr., 1900, i, 62, and Trans., 1891, **59**, 714) with dry sodium acetate and acetic anhydride, crystallises from alcohol in pale greyish-yellow needles.

3 : 5-*Diacetylaminophenazoxonium bromide*,

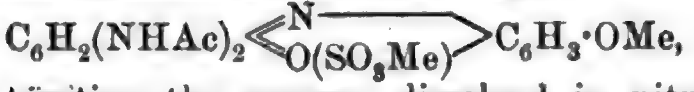


$$\mathrm{C_6H_4}<\!\!\begin{matrix}\mathrm{N}\\ \mathrm{OBr}\end{matrix}\!\!>\mathrm{C_6H_2(NHAc)_2},$$

prepared by treating an aqueous suspension of the preceding base successively with ferric chloride and sodium bromide, separates in small, steel-blue crystals; it is extremely reactive, being readily oxidised to *diacetylaminophenazoxone*,

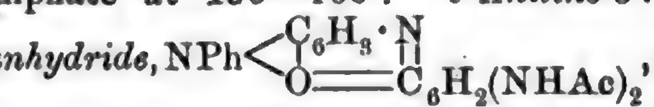


$\mathrm{O}<\!\!\begin{matrix}\mathrm{C_6H_3{\cdot}N}\\ \mathrm{O{=\!=}C_6H_2(NHAc)_2}\end{matrix}$, a substance crystallising in small, brown needles melting at 110—120°. 3 : 5-*Diacetylamino-9-methoxyphenazoxonium methosulphate*,

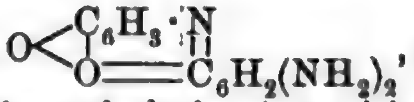


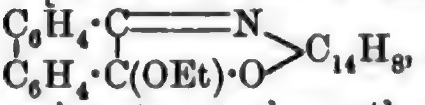
$$\mathrm{C_6H_2(NHAc)_2}<\!\!\begin{matrix}\mathrm{N}\\ \mathrm{O(SO_3Me)}\end{matrix}\!\!>\mathrm{C_6H_3{\cdot}OMe},$$

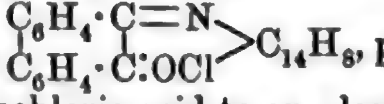
is obtained by treating the azoxone, dissolved in nitrobenzene, with dimethyl sulphate at 150—160°. 9-*Anilino*-3 : 5-*diacetylaminophenazoxonium anhydride*,

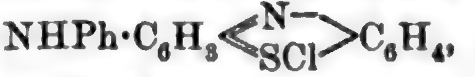
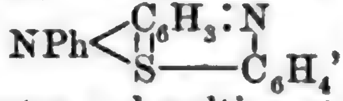


$\mathrm{NPh}<\!\!\begin{matrix}\mathrm{C_6H_3{\cdot}N}\\ \mathrm{O{=\!=}C_6H_2(NHAc)_2}\end{matrix}$, produced either from the bromide or the methyl sulphate by the action of an alcoholic solution of aniline, crystallises from a mixture of this solvent with benzene in dark red needles with a metallic lustre and melts at 273°.

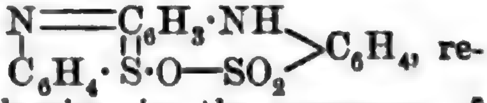
3 : 5-*Diaminophenazoxone*,  $O<\begin{matrix}C_6H_3\cdot N\\ O=\!=\!=C_6H_2(NH_2)_2\end{matrix}$, obtained by hydrolysing the corresponding diacetyl derivative with 50 per cent. sulphuric acid, crystallises from alcohol in long, green needles.

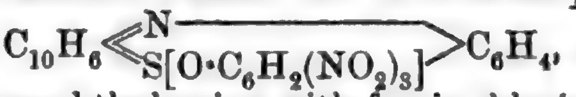
[With GEORG HERRMANN.]—*Ethyl phenanthrazoxonium ψ-oxide*,  $\begin{matrix}C_6H_4\cdot C=\!=\!=N\\ C_6H_4\cdot C(OEt)\cdot O\end{matrix}>C_{14}H_8$, results from the action of alcohol and sodium carbonate on phenanthrazoxonium perbromide (Abstr., 1901, i, 484); it crystallises from alcohol or benzene in lustrous, yellow needles, melting first at 245° and subsequently at 283°.

Phenanthrazoxonium chloride,  $\begin{matrix}C_6H_4\cdot C=N\\ C_6H_4\cdot C{:}OCl\end{matrix}>C_{14}H_8$, prepared by adding excess of concentrated hydrochloric acid to an alcoholic solution of the preceding compound, separates, with $3H_2O$, as a crystalline powder with a coppery reflex; it is insoluble in water and decomposed on boiling with alcohol.

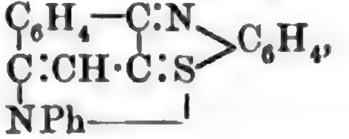
[With O. VESELÝ.] (Compare this vol., i, 186.)—3-*Anilinophenazothionium chloride*,  $NHPh\cdot C_6H_3<\begin{matrix}N\\ SCl\end{matrix}>C_6H_4$, produced by oxidising thiodiphenylamine with ferric chloride in the presence of aniline hydrochloride, separates in coppery needles; on treatment with alkaline solutions, it yields the anhydro-base,  $NPh<\begin{matrix}C_6H_3{:}N\\ S-\!-\!-C_6H_4\end{matrix}$, crystallising in dark red leaflets with a brass-like lustre and melting at 150°.

3 : 9-*Dianilinophenazothionium chloride* (*diphenylthionine chloride*), obtained by treating the preceding salt with aniline and alcohol, separates from this solvent in lustrous crystals.

Phenazothionium anhydro-3-sulphanilate,  $\begin{matrix}N=\!=\!=C_6H_3\cdot NH\\ C_6H_4\cdot S\cdot O-SO_2\end{matrix}>C_6H_4$, results from the oxidation of thiodiphenylamine in the presence of sodium sulphanilate; it separates as a greenish-black powder.

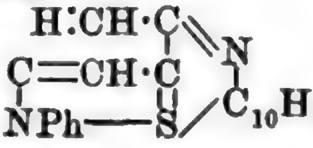
[With ALFRED GRESSLY and E. MISSLIN.]—α-*Naphthaphenazothionium picrate*,  $C_{10}H_6<\begin{matrix}N\\ S[O\cdot C_6H_2(NO_2)_3]\end{matrix}>C_6H_4$, prepared by oxidising thiophenyl-α-naphthylamine with ferric chloride in the presence of picric acid, separates in brown needles.

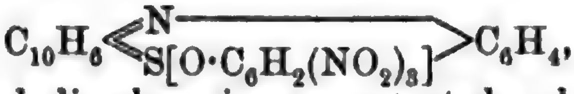
11-*Anilino-α-naphthaphenazothionium anhydride*,



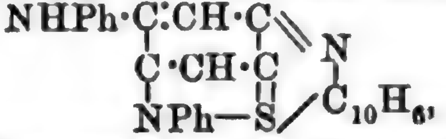
$$\begin{matrix}C_6H_4-C{:}N\\ C{:}CH\cdot C{:}S\\ NPh-\!-\!-\end{matrix}>C_6H_4,$$

produced by oxidising thiophenyl-α-naphthylamine in the presence of aniline hydrochloride, crystallises from alcohol or benzene in lustrous, brownish-red leaflets melting at 179°. Boiling dilute mineral acids hydrolyse the substance with the formation of salts.

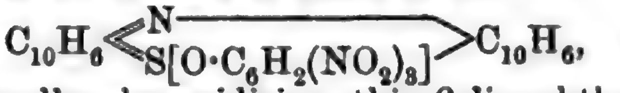
3-*Anilino-β-naphthaphenazothionium anhydride*,  $\begin{matrix}H{:}CH\cdot C\\ C=CH\cdot C\\ NPh-\!-\!-S\end{matrix}\begin{matrix}N\\ C_{10}H_6\end{matrix}$, obtained from thiophenyl-β-naphthylamine, crystallises from alcohol or benzene in lustrous, violet-brown leaflets melting at 175°; mineral acids hydrolyse it, yielding salts.

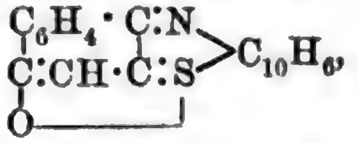
β-Naphthaphenazothionium picrate,  $C_{10}H_6<\genfrac{}{}{0pt}{}{N}{S[O\cdot C_6H_2(NO_2)_3]}>C_6H_4$, separates in small, green needles and dissolves in concentrated sulphuric acid to a violet-blue solution.

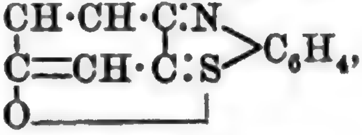
3 : 4-*Dianilino-β-naphthaphenazothionium anhydride*,

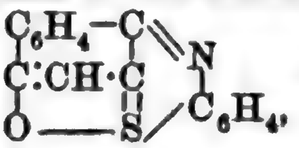


produced by boiling the preceding anhydride with an alcoholic solution of aniline hydrochloride, crystallises from benzene or alcohol in reddish-brown needles with a metallic reflex and melts at 229°.

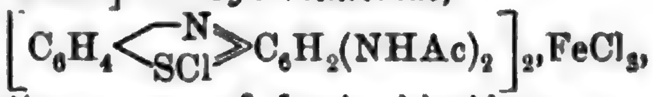
β Naphthazothionium picrate,  $C_{10}H_6<\genfrac{}{}{0pt}{}{N}{S[O\cdot C_6H_2(NO_2)_3]}>C_{10}H_6$, is obtained in small, dark-green needles by oxidising thio-β-dinaphthylamine with ferric chloride in the presence of picric acid. It was not found possible to obtain anilino-derivatives of β-naphthazothionium hydroxide either by oxidising thio-β-dinaphthylamine in the presence of aniline hydrochloride or by digesting the azothionium derivative with this salt.

Thio-α-dinaphthylamine, prepared by heating α-dinaphthylamine with sulphur at 230—240°, crystallises from alcohol in orange-yellow leaflets and melts at 176—177°; when oxidised, it gives rise to α-dinaphthazothionium derivatives, the *picrate* forms deep violet needles, whilst the anilino-derivative is unstable and is readily hydrolysed to *α-dinaphthazothione*,  a substance crystallising from alcohol or benzene in dark brown leaflets melting at 245°.

[With **Anatol Denguin**.]—*Phenazothione*,  formed by treating 3-aminophenazothionium chloride with sodium carbonate, is more readily prepared by oxidising thiodiphenylamine with a solution of ferric chloride in boiling dilute alcohol; it crystallises from benzene in reddish-brown leaflets and melts at 165—166°.

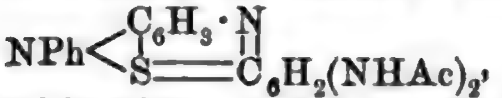
Phenonaphthazothione,  obtained by prolonged digestion of a dilute solution of α-naphthaphenazothionium sulphate at the ordinary temperature, separates from benzene in brownish-red crystals and melts at 176°.

[With **Leo Schild**.]—The *ferrichloride*,



$$\left[C_6H_4<\genfrac{}{}{0pt}{}{N}{SCl}>C_6H_2(NHAc)_2\right]_2,FeCl_3,$$

produced by adding excess of ferric chloride to an alcoholic solution of 3 : 5-diacetylaminothiodiphenylamine, is a dark green, crystalline precipitate, which readily gives rise to 3 : 5-*diacetylaminophenazothione*, $\mathrm{O}<\begin{array}{l}\mathrm{C_6H_3\cdot N}\\ \mathrm{S{=\!=}C_6H_2(NHAc)_2}\end{array}$, a substance separating in dark brown needles. This azothione readily undergoes hydrolysis, yielding 3 : 5-diaminophenazothione.

9-*Anilino*-3 : 5-*diacetylaminophenazothionium chloride* results from the action of aniline hydrochloride on the double ferric salt, and separates from alcohol or benzene in lustrous, granular crystals; the *anhydride*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{C_6H_3\cdot N}\\ \mathrm{S{=\!=}C_6H_2(NHAc)_2}\end{array}$, set free by ammonium carbonate crystallises from alcohol in reddish-brown needles and melts at 220—225°.

9-*Anilino*-3 : 5-*diaminophenazothionium chloride* separates in green granules with a metallic lustre on boiling the preceding anhydride with alcoholic hydrochloric acid; it is not affected by ammonia or alkali carbonates, but is decomposed by sodium hydroxide.

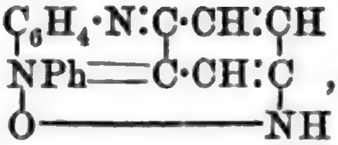
3 : 5-*Diacetylamino*-9-*methoxyphenazothionium methosulphate*,

$$\mathrm{OMe\cdot C_6H_3}<\begin{array}{r}\mathrm{N}\\ \mathrm{S(O\cdot SO_3Me)}\end{array}>\mathrm{C_6H_2(NHAc)_2},$$

produced by the action of dimethyl sulphate on 3 : 5-diacetylaminophenazothione in nitrobenzene solution at 150°, is a brown powder which yields the corresponding *dichromate*, $(C_{17}H_{16}O_3N_3S)_2Cr_2O_7$, by double decomposition with potassium dichromate; the sulphate is reconverted into 9-anilino-3 : 5-diacetylaminophenazothionium chloride by the successive action of aniline and hydrochloric acid.

[With Victor Veselý.]—*Resorcinolazodiphenyl aminesulphoxide*, $\mathrm{C_6H_4}<\begin{array}{c}\mathrm{NH}\\ \mathrm{SO}\end{array}>\mathrm{C_6H_3\cdot N_2\cdot C_6H_3(OH)_2}$, results from the action of diazotised 3-aminophenazothionium chloride on an aqueous solution of resorcinol containing sodium acetate; it crystallises from alcohol or benzene in reddish-yellow needles; a sparingly soluble bye-product separates out first from this mixture of solvents, which is probably a diazo-compound. The azo-derivative is insoluble in water, but on the addition of sodium hydroxide dissolves to a deep red solution; it develops a green coloration with concentrated sulphuric acid, this change being probably due to the formation of an unstable sulphate.

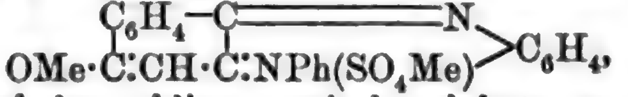
[With Hans Becker and Alexander Capatina.]—*Phenyldihydrophenazine*, $\mathrm{C_6H_4}<\begin{array}{c}\mathrm{NH}\\ \mathrm{NPh}\end{array}>\mathrm{C_6H_4}$, is prepared by reducing the phenylphenazonium ferrichloride obtained from picrylphenyl-*o*-phenylenediamine (Abstr., 1901, i, 52) with stannous chloride in dilute alcoholic solution; it crystallises from benzene in greyish-yellow leaflets, melts at 143°, and rapidly oxidises on exposure to the air, giving rise to aposaffranone (m. p. 248—249°); other oxidising agents produce the same effect. When only half the theoretical amount of reducing agent is employed in the preceding experiment, the solution assumes a green colour and contains an intermediate compound of the quinhydrone type which may be precipitated by sodium chloride and crystallised from alcohol in dark green prisms.

3-*Oxyaminophenylphenazonium anhydride*, 

$$\begin{array}{l} C_6H_4\cdot N{:}C\cdot CH{:}CH \\ NPh{=\!=}C\cdot CH{:}C \\ O\text{———————}NH \end{array}$$

, results from the action of hydroxylamine hydrochloride and sodium acetate on phenylphenazonium stannichloride dissolved in dilute alcohol; it separates from benzene or alcohol in dark red crystals, dissolves in glacial acetic acid, and develops a green coloration with concentrated sulphuric acid (compare Abstr., 1899, i, 82, and Fischer and Hepp, Abstr., 1901, i, 463).

11-*Methoxy*-1-*phenylnaphthaphenazonium methosulphate*,



$$\begin{array}{l} \quad\;\; C_6H_4-C\text{═══════}N \\ OMe\cdot C{:}CH\cdot C{:}NPh(SO_4Me) \end{array} \!\!> C_6H_4,$$

is readily obtained by adding methyl sulphate to a nitrobenzene solution of rosindone at 150° and diluting the product with ether; it crystallises in orange-yellow needles; the corresponding *bromide*, prepared by double decomposition, separates in golden-yellow leaflets soluble in water or alcohol. The *platinichloride* precipitated from an aqueous solution of the methyl sulphate on the addition of chloroplatinic acid forms brick-red crystals, developing with concentrated sulphuric acid a purple coloration. The bromide, when treated with an alcoholic solution of ammonia or aniline, gives rise to rosinduline or phenylrosinduline respectively, the former being identical with the product of the action of 4-amino-β-naphthaquinone on phenyl-*o*-phenylene hydrochloride. G. T. M.

Nitrosoacylphenylhydrazines. By HUGO VOSWINCKEL (*Ber.*, 1902, **35**, 1943—1947).—Nitrosobenzoylphenylhydrazine dissolves in dilute aqueous sodium hydroxide, but on adding an excess of the alkali, crystals of the *sodium* derivative, NO·NPh·NNa·COPh, separate; this can be recrystallised from acetone, and by methyl iodide is converted into *a-nitroso-β-benzoyl-a-phenyl-β-methylhydrazine*, NO·NPh·NMe·COPh, which forms stout, yellowish prisms, melts at 108°, and is reduced in alcoholic solution by stannous chloride and hydrochloric acid to *β-benzoyl-a-phenyl-β-methylhydrazine*, NHPh·NMe·COPh. The latter crystallises from dilute alcohol, melts at 136°, and is converted by benzoyl chloride into $a\beta$-dibenzoyl-a-phenyl-β-methylhydrazine (Tafel, Abstr., 1885, 1060), a fact which proves its structure.

The *silver* derivative, NO·NPh·NAg·COPh, corresponding with the foregoing sodium compound, is unstable and decomposes almost immediately after being precipitated; an attempt to replace the metal by alkyl groups gave only benzoylazobenzene, NPh:N·COPh, which is converted by concentrated hydrochloric acid into benzoyl-*o*-chlorophenylhydrazine, $C_6H_4Cl\cdot NH\cdot NH\cdot COPh$ (Hantzsch and Singer, Abstr., 1897, i, 216).

1-Phenylbenzothiazole is formed on fusing benzoylphenylhydrazine with sulphur. W. A. D.

Additive Compounds of Aldehydes with Phenylhydrazine-*p*-Sulphonic Acid. By HEINRICH BILTZ, A. MAUÉ, and FR. SIEDEN (*Ber.*, 1902, **35**, 2000—2008).—Phenylhydrazine-*p*-sulphonic acid combines with a number of aldehydes forming somewhat unstable additive compounds of the type $OH\cdot CHPh\cdot NH\cdot NH\cdot C_6H_4\cdot SO_3H$, which can often be obtained in a crystalline form by the addition of the aldehyde to the sulphonic acid in the presence of a small amount of water. They are mostly yellow compounds, soluble in water and somewhat readily decomposed by water, especially when boiled. Decomposition occurs more readily when the compounds are boiled with dilute acids. The sodium salts are colourless or pale yellow, and may be crystallised from warm water. The formation of substituted phenylhydrazones by the elimination of water has not been observed.

The stability of the compounds increases with the presence of negative groups, for example, nitro- and hydroxyl groups, in the aldehyde molecule; whereas positive groups, for example, aryl groups, tend to diminish the stability.

Benzaldehydephenylhydrazone-p-*sulphonic acid hydrate* decomposes at about 95°. The compound from salicylaldehyde decomposes at about 110°; that from anisaldehyde sinters at 120° and melts and decomposes at 155—165°. m-*Nitrobenzaldehydephenylhydrazone*-p-*sulphonic acid hydrate* decomposes between 80° and 90°. The compounds with cuminaldehyde, cinnamaldehyde, and valeraldehyde are so unstable that they could not be obtained pure. J. J. S.

Method of Isolating Aldehydes and Ketones. By Carl Neuberg and W. Neimann (*Ber.*, 1902, **35**, 2049—2056).

—The thiosemicarbazones of aldehydes and ketones readily yield insoluble copper, silver, and mercury derivatives, which can be used for the purpose of isolating these compounds. These salts are formed when alcoholic solutions of a salt of the metals and a thiosemicarbazone are mixed; the copper and silver salts are amorphous, whilst the mercury salts are crystalline.

Valeraldehydethiosemicarbazone, $C_4H_9\cdot CH:N\cdot NH\cdot CS\cdot NH_2$, prepared by adding a concentrated aqueous solution of thiosemicarbazide to an alcoholic solution of valeraldehyde, is crystalline and melts at 65°; the *silver* salt is obtained as an amorphous powder when an alcoholic solution of silver nitrate is added to an alcoholic solution of the thiosemicarbazone. iso*Valeraldehydethiosemicarbazone* melts at 52—53° and gives a *silver* salt. *Heptaldehydethiosemicarbazone* forms crystals and yields a *silver* salt. *Acetophenonethiosemicarbazone*, melts at 108° and yields a *silver* salt. *Piperonalthiosemicarbazone* melts at 185° and becomes rose-coloured in the air; the *silver* salt is a very stable powder. *Citronellalthiosemicarbazone* melts at 54—55°, and *menthonethiosemicarbazone* crystallises in needles melting at 155—157°. *Glyoxaldithiosemicarbazone* is obtained from glyoxal and thiosemicarbazide, or less easily from trichlorolactic acid and the semicarbazide; it crystallises in yellowish needles decomposing above 300°, is soluble in dilute alkalis or alkali carbonates, and forms a yellowish-green, amorphous *silver* salt. The *thiosemicarbazone* of *d*-dextrose crystallises in rhombic plates melting at 204°, that of *d*-mannose melts at 187°, and that of *d*-galactose at 148°; the latter crystallises in long needles. The thiosemicarbazones of the sugars do not yield silver salts. *d*-Glucuronthiosemicarbazone yields a *silver* salt,

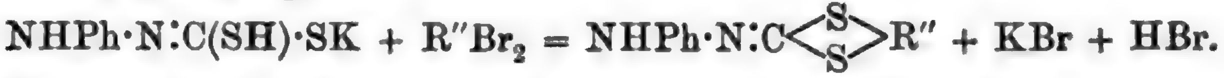
$$NH_2\cdot C(SAg):N\cdot N\cdot CH\cdot[CH\cdot OH]_4\cdot CO_2Ag,$$

the lactone ring being opened.

The thiosemicarbazones are readily obtained from the silver salts by decomposing them with hydrogen sulphide in the presence of alcohol or ether; the aldehyde or ketone can be recovered from the thiosemicarbazone by the action of mineral acids or by heating them with phthalic anhydride.

The view is expressed that in these salts the metallic atom is attached to the sulphur atom. K. J. P. O.

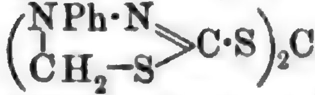
Limits of the Formation of Cyclic Dithiocarbonates. By Max Busch and Edmund Lingenbrink (*J. pr. Chem.*, 1902, [ii], **65**, 473—479).—In certain cases (Abstr., 1900, i, 66, 411), it has been shown that a dithiocarbazinate reacts with a dihaloid to form the hydrazone of a cyclic dithiocarbonate. Potassium dithiocarbazinate is now shown to react in this way with trimethylene or *o*-xylylene dibromide, as well as with ethylene dibromide; a ring is formed containing six, seven, or five atoms respectively, and the reaction is represented by the equation



$$\mathrm{NHPh{\cdot}N{:}C(SH){\cdot}SK + R''Br_2 = NHPh{\cdot}N{:}C{<}\begin{matrix}S\\S\end{matrix}{>}R'' + KBr + HBr.}$$

In the case of methylene and pentamethylene dibromides, where a similar reaction would result in the formation of rings containing four and eight atoms respectively, quite a different reaction occurs; the dithiocarbazinate reacts in the tautomeric form, yielding an ester which differs from the cyclic compounds in possessing acid properties; the equation is $\mathrm{2NHPh{\cdot}NH{\cdot}CS_2K + R''Br_2 = (NHPh{\cdot}NH{\cdot}CS_2)_2R'' + 2KBr}$. In all cases, the reaction was allowed to take place in dilute alcoholic solution at the ordinary temperature.

Of the *phenylhydrazones* of cyclic *dithiocarbonates*, the *trimethylene*, $[\mathrm{R''=CH_2(CH_2{\cdot})_2}]$, and *o-xylylene*, $[\mathrm{R''=C_6H_4(CH_2{\cdot})_2}]$, derivatives melt at 76° and 202° respectively; the melting point of the ethylene derivative, $[\mathrm{R''=CH_2{\cdot}CH_2}]$, is now found to be 92°, not 94° (Abstr., 1894, i, 625) or 88° (Miolati, Abstr., 1891, 895).

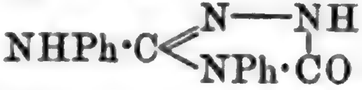
Methylene phenyldithiocarbazinate, $(\mathrm{R''=CH_2})$, melts at 167°; when boiled with aqueous formaldehyde, it condenses (compare Abstr., 1899, i, 825, 950) to the methylene ester of *phenylthiodiazolinethiol*,  $\left(\begin{matrix}\mathrm{NPh{\cdot}N}\\ \vert\\ \mathrm{CH_2{-}S}\end{matrix}{>}\mathrm{C{\cdot}S}\right)_2\mathrm{CH_2}$, which melts at 123—124°. *Pentamethylene phenyldithiocarbazinate*, $[\mathrm{R''=CH_2(CH_2{\cdot}CH_2{\cdot})_2}]$, melts at 140—141°.

C. F. B.

Aminoguanidines. By Max Busch and Th. Ulmer (*Ber.*, 1902, **35**, 1716—1726).—The *acid oxalate*, $\mathrm{C_{13}H_{14}N_4,C_2H_2O_4}$, obtained by mixing ethereal solutions of aminodiphenylguanidine and oxalic acid, melts and decomposes at 147°; when crystallised from alcohol, it is converted into the normal salt, and when heated alone at 160° it yields, by loss of water and carbon dioxide, 5-anilino-4-phenyltriazole (Busch and Bauer, Abstr., 1900, i, 414). On adding carbon disulphide to aminodiphenylguanidine dissolved in ether, the *salt*,

$$\mathrm{C_{13}H_{13}N_4{\cdot}CS{\cdot}SH,C_{13}H_{14}N_4},$$

of the corresponding dithiocarbazinic acid is obtained as a yellowish-white, crystalline powder. With phosgene dissolved in toluene, aminodiphenylguanidine gives 3-*anilino-4-phenyl-5-triazolone*,

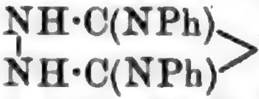
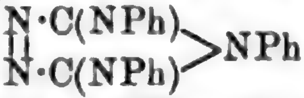
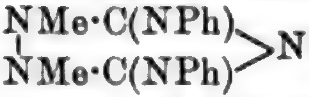


$$\mathrm{NHPh{\cdot}C}{<}\begin{array}{l}\mathrm{N{-\!-}NH}\\ \mathrm{NPh{\cdot}CO}\end{array},$$

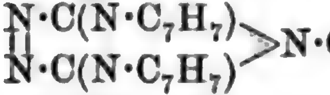
which crystallises from dilute alcohol in long, colourless needles and melts at 212—213°; with benzil, the *hydrazone*,

$$\mathrm{NPh{:}C(NHPh){\cdot}NH{\cdot}N{:}CPh{\cdot}COPh},$$

is obtained in the form of small, yellow prisms melting at 163—164°.

When aminodiphenylguanidine is heated at 180°, it loses aniline and hydrazine hydrate and is converted into *triphenylguanazole* (3:5-*dianil-4-phenylurazole*),  $\begin{array}{l}\mathrm{NH{\cdot}C(NPh)}\\ \mathrm{NH{\cdot}C(NPh)}\end{array}{>}\mathrm{NPh}$, which crystallises from alcohol in large leaflets with $2C_2H_6O$, melts at 234°, yields a crystalline *hydrochloride*, $C_{20}H_{17}N_5,HCl$, melting at 127°, and is oxidised by alcoholic mercuric oxide, bromine water, or potassium permanganate, to the *azo*-compound,  $\begin{array}{l}\mathrm{N{\cdot}C(NPh)}\\ \mathrm{N{\cdot}C(NPh)}\end{array}{>}\mathrm{NPh}$; this forms blackish-brown, slender needles and melts at 192°. *Dimethyltriphenylguanazole*,  $\begin{array}{l}\mathrm{NMe{\cdot}C(NPh)}\\ \mathrm{NMe{\cdot}C(NPh)}\end{array}{>}\mathrm{NPh}$, obtained by methylating the base, crystallises from alcohol in sheaves of prisms and melts at 182°; the analogous *diethyl* compound melts at 159—160°; *diacetyltriphenylguanazole* separates from glacial acetic acid in aggregates of stout prisms and melts at 218°.

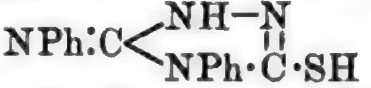
Tetraphenylhydrazodicarbonamidine, $N_2H_2[C(NHPh){:}NPh]_2$, is no doubt the intermediate product formed from aminodiphenylguanidine in the production of triphenylguanazole, as it is converted into the latter by loss of aniline when heated alone at 200° or when boiled with concentrated hydrochloric acid; it is best obtained by adding carbodiphenylimide in benzene solution to aminodiphenylguanidine or to hydrazine hydrate, and crystallises from alcohol in silky, efflorescent needles melting at about 164—165°.

Tri-p-*tolylguanazole* (3:5-*ditolil-4-tolylurazole*), obtained by heating *aminodi*-p-*tolylguanidine* at 200°, crystallises from alcohol in colourless leaflets, melts at 223—224°, and forms a *hydrochloride*, $C_{23}H_{23}N_5,HCl$, melting at about 105°; the *diacetyl* compound, $C_{27}H_{29}O_2N_5$, is granular and melts at 175°. Nitrous acid converts the guanazole dissolved in alcohol into *tri*-p-*tolyldehydroguanazole*,  $\begin{array}{l}\mathrm{N{\cdot}C(N{\cdot}C_7H_7)}\\ \mathrm{N{\cdot}C(N{\cdot}C_7H_7)}\end{array}{>}\mathrm{N{\cdot}C_7H_7}$, which crystallises in violet-blue needles, melts at 178°, and is also obtained by the action of bromine water or permanganate on the guanazole; it is reconverted into the latter by hydrogen sulphide.

Aminodi-o-anisylguanidine,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}N{:}C(NH{\cdot}C_6H_4{\cdot}OMe){\cdot}NH{\cdot}NH_2},$$

obtained by heating dianisylthiocarbamide with hydrazine hydrate and alcoholic potassium hydroxide for 4 hours at about 100°, is a syrup which yields a crystalline *picrate* melting at 154°. *Aminodi-β-naphthylguanidine*, prepared from di-β-naphthylcarbamide, crystallises from alcohol or benzene in needles, melts at 163—164°, and yields a *hydrochloride*, $C_{21}H_{18}N_4,HCl,H_2O$, melting at 145°; the *nitrate* melts at 95—96°, and the *picrate* at 196—197° with decomposition. *Tri-β-naphthylguanazole* crystallises from alcohol in soft needles and melts at 216°. W. A. D.

Products of the Interaction of Hydrazine with Thiocarbamides. II. By Max Busch and Th. Ulmer (*Ber.*, 1902, **35**, 1710—1716).—When thiocarbanilide is heated with hydrazine hydrate and only a small proportion of alcoholic potash for four hours at 130—135°, 4-*phenyl*-5-*aniltriazolone*-3-*thiol*,  $\mathrm{NPh{:}C}<\begin{matrix}\mathrm{NH-N}\\ \mathrm{NPh\cdot\overset{\|}{C}\cdot SH}\end{matrix}$, is the principal product instead of aminodiphenylguanidine (Abstr., 1900, i, 414); it is formed from the latter by the action of thiocarbanilide, thiocarbanilinoaminodiphenylguanidine being produced as an intermediate product, and can also be obtained by the interaction of aminodiphenylguanidine and phenylthiocarbimide. It crystallises from alcohol in sheaves of colourless prisms and melts at 206°; the *potassium* salt forms colourless leaflets melting at 125—126°, and the *methyl* and *ethyl ethers* long needles melting at 226—227° and 214—215° respectively. 4-*Phenyl*-5-*aniltriazolone* 3-*disulphide*, $C_{28}H_{22}N_8S_2$, obtained by oxidising the thiol with hydrogen peroxide or iodine, crystallises from alcohol in yellow needles and melts at 209—210°. If the potassium salt of the thiol be oxidised with alkaline hydrogen peroxide, 5-anilino-5-phenyltriazole (*loc. cit.*) is obtained.

In alcoholic solution in absence of alkali, diarylthiocarbamides of the type $NHR\cdot CS\cdot NHPh$ with hydrazine hydrate yield exclusively arylsemicarbazides, but a similar law does not hold for mixed aliphatic aromatic thiocarbamides.

4-p-*Tolylthiosemicarbazide*, $C_7H_7\cdot NH\cdot CS\cdot NH\cdot NH_2$, crystallises from benzene in silvery leaflets melting at 134—135° and 4-p-*anisylthiosemicarbazide* in large leaflets melting at 144°. 4-p-*Chlorophenylthiosemicarbazide* melts at 180° and 4-*a-naphthylthiosemicarbazide* at 138—139°.

Phenylethylthiocarbamide is not attacked by alcoholic hydrazine hydrate at 100°. Attempts to prepare aminoguanidines from dibenzoyl thiocarbamide or diphenylbenzylthiocarbamide by the action of alcoholic hydrazine hydrate and potassium hydroxide at 130—135° also gave negative results. W. A. D.

New Decompositions of the Diazo-compounds. By Joachim Biehringer and Albert Busch (*Ber.*, 1902, **35**, 1964—1976).—The principal product of the action of copper powder on a mixture of benzenediazonium chloride and benzoyl chloride is *dibenzoylhydrazobenzene*, $COPh\cdot NPh\cdot NPh\cdot COPh$; this, which was also prepared synthetically from hydrazobenzene, crystallises from alcohol in prisms or in pearly plates and melts at 161°. The isomeric dibenzoylbenzidine crystallises from nitrobenzene or from phenol in colourless prisms and melts at 352°. *Dibenzoyldiphenyline*, another isomeride, crystallises from nitrobenzene in microscopic forms and melts at 277°.

Monobenzoyl-o-aminodiphenylamine separates from wood spirit in colourless, monoclinic prisms. *Dibenzoyl*-p-*aminodiphenylamine* crystallises from wood-spirit in rectangular tablets and melts at 203° (uncorr.).

*Dibenzoyl-*p*-hydrazotoluene*, $C_{28}H_{24}O_2N_2$, prepared by two similar methods, crystallises from light petroleum in colourless, silky plates and melts at 157°.

Dibenzoyl-o-hydrazotoluene crystallises from much hot water in colourless needles and melts at 144° (uncorr.). The isomeric *dibenzoyl-o-tolidine* is insoluble in most solvents except the organic bases, from which it separates on adding alcohol in colourless, microscopic needles melting at 265°. T. M L.

Coupling of Toluidines with Diazo-compounds. By HANS MEHNER (*J. pr. Chem.*, 1902, [ii], **65**, 401—472).—Many examples were found of the long known fact that the same diazoamino-compound, $X·N_3H·Y$, is obtained, whether $X·N_2·Cl$ and $Y·NH_2$, or $Y·N_2·Cl$ and $X·NH_2$, be the diazochloride and amine which are coupled. Further, in the coupling of *p*- and *m*-diazotoluene with aniline and of *p*-diazotoluene and *p*- and *m*-nitrodiazobenzene with *p*-toluidine, that is, in cases where the amine to be coupled is either aniline or a para-substituted aniline, only a diazoamino-compound is obtained. In other cases, a mixture is obtained of diazoamino- with aminoazo-compound in varying proportions. The presence of hydrogen ions appears to accelerate the transformation of diazoamino- into aminoazo-compound, for a larger yield of the former is obtained if sodium hydrogen carbonate instead of sodium acetate is added to the mixture of diazochloride and amine hydrochloride, and the yield is still larger if the solid diazo-salt is added to a cooled solution of the amine in pyridine and the product finally precipitated with ice and water. The last method was particularly efficacious when the amine was *m*-toluidine; in coupling this in pyridine solution with diazobenzene salt, the yield of diazoamino-compound was 90 per cent. of the whole, whereas it was only 40 per cent. when the coupling was effected in aqueous solution and sodium acetate was added. The use of sodium hydrogen carbonate has a disadvantage in cases where the amine only reacts slowly with the diazo-salt, for then the amine is largely thrown out of solution, and before all the diazo-salt has reacted with the amine some of it usually decomposes to a phenol which then couples with more of the diazo-salt to an hydroxyazo-compound. In this operation, a migration of the diazo-group from one radicle to the other must often occur, for only on this supposition is it possible to account for the constitution of the hydroxyazo-derivatives that are formed. In order to find the structure of the diazoamino-compounds, $X·N⁚N·NH·Y$ (compare Goldschmidt, Abstr., 1888, 685, 1283), additive products of these with phenylcarbimide, $NHPh·CO·NY·N⁚NX$, were prepared in ethereal solution, and these carbamide derivatives were hydrolysed by boiling their solutions in alcohol or 10 per cent. sulphuric acid, whereby a carbamide, $NHPh·CO·NHY$, is obtained. From the constitution of this carbamide, that of the original diazoamino-compound is inferred; it would have been $Y·N⁚N·NH·X$ had the carbamide $NHPh·CO·NHX$ been obtained. The two isomeric *p*-nitrobenzenediazoamino-*p*-toluenes (Bamberger, Abstr., 1895, i, 351) were examined, and the superior stability of the red modification is attributed to the fact that its crystals are larger than those of the yellow modification, and consequently have a relatively smaller surface and smaller solubility. A similar case of isomerism was discovered in the case of *p*-nitrobenzenediazoamino-*o*-toluene.

Hydroxyazo-compounds were formed in the following cases. *p*-Hydroxyazobenzene from diazobenzene with *o*-toluidine. 4-Hydroxy-3 : 2′-dimethylazobenzene, 4-hydroxy-2 : 2′ : 2″-trimethyl-1 : 5-disazobenzene, $OH\cdot C_6H_2Me(N⁚N\cdot C_6H_4Me)_2$, and 4-hydroxy-3 : 4′-dimethylazobenzene (migration) from *o*-diazotoluene and *p*-toluidine. *4′-Nitro-2-hydroxy-5-methylazobenzene* (migration), melting at 186·5°, from *p*-nitrodiazobenzene and *p*-toluidine. 4′-Nitro 4-hydroxy-3-methylazobenzene (migration) from *p*-nitrodiazobenzene and *o*-toluidine.

The following are the other new compounds prepared, with their melting points. *Benzenediazoamino-m-toluene*, $C_6H_4Me\cdot N⁚N\cdot NHPh$, 86°; additive *carbamide*, 116°. *Benzeneazotoluenes* : m-, 76°; o-, 118—119°. *Diazoaminotoluenes*, $C_6H_4Me\cdot N⁚N\cdot NH\cdot C_6H_4Me$:— *m* : *p*, 96—97°; additive *carbamide*, 115°; *o* : *p*, 119—120°; additive *carbamide*, 117—118° (phenyl-*o*-tolylcarbamide melts at 196°, *not* 212°); contrary to the usual rule, the phenylcarbimide has added itself to the less negative radicle; *m* : *m*, 50—52°; *o* : *m*, 74°, additive *carbamide*, about 117°. *4-Amino-3 : 3′-dimethylazobenzene*, 124°; 4 : 2 : 2′, 116—117°. *Nitrobenzenediazoaminotoluenes* :—*p* : *m* 138°; *p* : *o*, 135°, 139°; *m* : *m*, 89—92°; *m* : *o*, 110—111°; *o* : *p*, 112·5°; *o* : *m*, 113—115; *o* : *o*, 134—135. *Nitroaminomethylazobenzenes* :—4′ : 4 : 2, 152—153; 4′ : 4 : 3, 195—197°; 3′ : 4 : 2, 172°; 3′ : 4 : 3, 151—152°; 2′ : 4 : 2, 119—121°; 2′ : 4 : 3, 99°.

C. F. B.

A New System of Classification of Azo-dyes. By Hans Bucherer (*Chem. Centr.*, 1902, i, 917; from *Zeit. Farben. Textilchem.*, 1902, 1, 8—10, 45—46, 150—152).—The following system of indicating the composition of azo-dyes is not based on any scientific principle, but is devised simply for convenience of reference. The formula of azobenzene is written b·b, and in the case of substitution products the number of substituting groups in each benzene ring is shown by affixing a number thus, aminoazobenzene $b\cdot b_1$; aminoazobenzenesulphonic acid, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_6H_4NH_2, b_1\cdot b_1$; aminoazobenzenedisulphonic acid, $(SO_3H)_2\cdot C_6H_3\cdot N_2\cdot C_6H_4NH_2, b_1\cdot b_2$. The naphthalene ring or residue is indicated by n, and the diphenyl residue by B. The dye prepared from toluidine, salicylic acid, and aminonaphthalenesulphonic acid, for instance, is written $b_2\cdot B_2\cdot n_3$. This system allows of the use of a great number of symbols, which, when arranged in accordance with mathematical principles, considerably simplifies the process of identifying any azo-dye. By way of example, the system has been applied to the dyes contained in Schultz and Julius' summary (3 *Auflage*, 1897).

E. W. W.

Phenylazoacetaldoxime and Voswinckel's Triazan Derivatives. By Eugen Bamberger (*Ber.*, 1902, **35**, 1896—1900. Compare Voswinckel, this vol., i, 321).—It is urged that phenylazoacetaldoxime has the formula $NOH⁚CMe\cdot N⁚NPh$, and is not a pseudo-acid of the formula $NO\cdot CHMe\cdot N{:}NPh$; it alters the ratio of distribution of ammonia between toluene and air in favour of the former and behaves altogether like benzaldoxime.

Its reduction product, $C_8H_{11}N_3$, is probably $NH{:}CMe\cdot NH\cdot NHPh$ or $NH_2\cdot CMe{:}N\cdot NHPh$, and not $CHMe<\begin{matrix}NH\\NH\end{matrix}>NPh$, and all the compounds described by Voswinckel (*loc. cit.*) as derivatives of triazan can be better formulated as open-chain compounds not containing a triazine-group. T. M. L.

Derivatives of Phenyltriazan. By Alfred Wohl and Hans Schiff (*Ber.*, 1902, **35**, 1900—1904).—*Acetylformylphenylbenzylidenetriazan*, $CHO\cdot NAc\cdot NPh\cdot N{:}CHPh$, prepared by the action of acetyl chloride and acetic anhydride on formylphenylbenzylidenetriazan, crystallises from alcohol in brilliant, white needles and melts at 125°. *Acetylphenylbenzylidenetriazan*, $NHAc\cdot NPh\cdot N{:}CHPh$, prepared by boiling the preceding compound with alcoholic potash, crystallises from 50 per cent. alcohol in white needles and melts and decomposes at 162—164°. *Nitrosoacetylphenylhydrazine*, $NO\cdot NPh\cdot NHAc$, melts and decomposes at 63° and is readily soluble in alcohol; when reduced and then condensed with benzaldehyde, it gives the acetylphenylbenzylidenetriazan just described; the alcoholic solution of the reduction product can be evaporated under reduced pressure without decomposition, but is decomposed on adding water and extracting with ether.

T. M. L.

Fatty Aromatic Aminoazo-compounds. II. By Bernh. Prager (*Ber.*, 1901, **35**, 1862—1866. Compare this vol., i, 64).—The compound, $C_{20}H_{22}O_5N_4$, which is formed by the union of *p*-nitrobenzaldehyde with ethyl benzenazomethylaminocrotonate, appears to be *ethyl δ-hydroxy-a-phenylazo-β-methylimino-δ-*p*-nitrophenylvalerate*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot C(NMe)\cdot CH(CO_2Et)\cdot N{:}NPH$. When heated with dilute acetic acid alone, it loses methylamine, forming *ethyl a-phenylazo-δ-nitrophenylpentane-δ-ol-β-one-carboxylate*,

$$NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot CO\cdot CH(CO_2Et)\cdot N{:}NPh,$$

which crystallises in stellate groups of faintly yellow needles, melting at 147—148° (corr.). Alcoholic sulphuric acid converts both this compound and the original substance into *a-phenylazo-δ-*p*-nitrophenylpentane-β-one-aδ-olide*, $O<\begin{matrix}CH(C_6H_4\cdot NO_2)\cdot CH_2\\CO\text{——}CH(N{:}NPh)\end{matrix}>CO$, alcohol and methylamine being eliminated; this substance decomposes at about 218° (corr.) and has the properties of a lactone, since it is insoluble in alkalis in the cold but dissolves on being heated.

In agreement with the constitution which is here assigned to it, the compound $C_{20}H_{22}O_5N_4$ yields 1 mol. of aniline on reduction, whilst there is no formation of *ethyl a-aminoacetoacetate*. A. H.

Fractional Precipitation of Proteids by Salts. By Jean Effront (*Chem. Centr.*, 1902, i, 1113; from *Mon. Sci.*, [iv], **16**, 241—254).—In spite of its disadvantages, the fractional precipitation of proteids with salts like ammonium sulphate and zinc sulphate is recommended as trustworthy for their separation. W. D. H.

Silk Glue—Sericin. By S. Bondi (*Zeit. physiol. Chem.*, 1902, **34**, 481—499. Compare Cramer, *J. pr. Chem.*, 1865, **96**, 76; Bolley, *ibid.*, 1869, **108**, 364).—The sericin was obtained by a slightly modified form of Mulder's method (*Ann. Phys. Chem.*, 1836, **37**, 594), and after prolonged extraction with distilled water contained 2·13 per cent. of ash. C = 45·01; H = 6·32; N = 17·15 per cent. The pure compound is completely soluble in water, but concentrated solutions (2 per cent.) have a somewhat cloudy appearance. This soluble form is readily transformed into a sparingly soluble modification under the influence of heat, by evaporation under reduced pressure, and by action of dilute acids. Concentrated hydrochloric acid readily dissolves sericin, concentrated nitric acid only slowly, and concentrated sulphuric acid dissolves it after continuous shaking for 24 hours. Glacial acetic acid dissolves it only slowly and incompletely. Dilute acids (5 per cent. solutions) produce "swelling" at the ordinary temperature, but at 90° dissolve the glue. Sericin dissolves very readily in dilute potassium hydroxide, but not in dilute sodium hydroxide. Most of the resulting solutions contain primary albumoses. A tabular statement of the behaviour of aqueous sericin solutions under different conditions is given. J. J. S.

Combination of Formaldehyde with Witte's Peptone. By Torald Sollmann (*Amer. J. Physiol.*, 1902, **7**, 220—242).—The addition of formaldehyde to a feebly alkaline solution of Witte's peptone causes the slow development of a precipitate. It is soluble on boiling with dilute acid or alkali, but prolonged contact with the precipitant causes a lessening of its solubility. The solutions give the general reactions of the original proteose and may be reprecipitated by dilute alkali. The precipitate contains both chemically combined and mechanically retained formaldehyde. Only about 40 per cent. of the proteids present participate in the reaction; the primary proteoses are completely precipitated. The formation of the precipitate occurs within narrow limits of reaction, the optimum being 1·1 c.c. normal alkali per gram. In an acid liquid, no combination, and so no precipitation, occurs. Increased alkalinity favours the combination, but as the compound is soluble in alkaline liquids, precipitation is prevented. The formaldehyde and the alkali both enter into the combination in a constant ratio and are liberated in their original quantities by the action of acid. The combination is prevented by the presence of neutral salts.

One gram of Witte's peptone combines with 0·0447 gram of formaldehyde and 6·4 c.c. of decinormal alkali. One gram of the compound contains 0·1109 gram of formaldehyde and 15·9 c.c. of decinormal alkali. The ratio of formaldehyde to alkali is, thus, two equivalents of the former to one of the latter. Since the combined alkali is probably the natural alkalinity of the proteose, it follows that one equivalent of proteose unites with two of formaldehyde. A combination with alkali is also seen with other proteids (compare Benedicenti, *Arch. Physiol.*, 1897, 219, 223). Acacia [*sic.* ? Arabin] does not combine with formaldehyde.

W. D. H.

Hydrogenases: New Case of Diastatic Hydrogenation. By M. EMM. POZZI-ESCOT (*Bull. Soc. Chim.*, 1902, [iii], **27**, 346—349).—For the purpose of determining whether philothion really possesses the power of hydrogenation, the author has carried out several quantitative experiments on its action on sulphur, whereby he proves that formation of hydrogen sulphide certainly takes place; in the case of selenium and phosphorus, hydrogenation could also be observed, but not, or scarcely so, in the case of arsenic and tellurium. It is also shown that hydrogenases and oxydases mutually decompose one another, a fact which the author holds to plausibly explain the destruction of œnooxydase in vinous fermentation. A. F.

Formation of Oxidation Ferments (Tyrosinase) by Bacteria. By KARL B. LEHMANN (*Chem. Centr.*, 1902, i, 770; from *Münch. med. Woch.*, **49**, 340).—The brown colour of the nutritive medium in which bacteria, such as, for instance, *Bacillus fluorescens non liquefaciens*, has been cultivated, is due to the presence of tyrosinase. When the medium contains sugar, however, it does not become brown. The assumption that by the action of bacteria tyrosine is formed when sugar is not present, and that the tyrosine is then attacked by an oxydase, is supported by the facts that the addition of tyrosine to a culture containing sugar caused it to become brown, and that the colour of a culture free from sugar was intensified by the addition of tyrosine. E. W. W.

Yeast Trypsin. II. By FR. KUTSCHER (*Zeit. physiol. Chem.*, 1902, 517—519).—Polemical. Replies to (I) Salkowski (this vol., ii, 165), in which it is stated that the observations made by Salkowski had been previously made by Schützenberger; (II) Hahn and Geret (Abstr., 1901, ii, 677). J. J. S.

Formation of Zymase in Yeast. By EDUARD BUCHNER and ALBERT SPITTA (*Ber.*, 1902, **35**, 1703—1706).—It has been found by Albert (Abstr., 1899, ii, 783) that when yeast is placed in a 10 per cent. solution of sugar free from nitrogenous nourishment, it yields a more active juice than the unregenerated yeast. If, however, the yeast be taken from the regenerating liquid at the period of most intense fermentation, the juice obtained is less active than that obtained from the original yeast. It has also been found that the amount of zymase contained in yeast decreases when the yeast is preserved in a warm place, but increases when the temperature is kept low. By taking samples of yeast at various times and immediately treating them with alcohol and ether, and then estimating the fermenting power of the yeast as described by Albert, the author finds that when the yeast is exposed to sugar solution for 4—8 hours its fermenting power diminishes, but if it be then pressed and preserved for 2—3·5 hours at a low temperature (0—8°) it increases considerably, in one case by 35 per cent. and in another by 64 per cent. A. H.

Organic Chemistry.

Synthesis of Various Petroleums; Theory of the Formation of Natural Petroleums. By Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1902, **134**, 1185—1188).—The action of reduced nickel on a mixture of acetylene and hydrogen at a temperature not exceeding 200° yields a highly fluorescent mixture of hydrocarbons which is only slightly attacked by a mixture of nitric and sulphuric acids and has the general physical properties of American petroleum.

If acetylene alone is allowed to act on nickel heated at about 200°, products are formed in the cooler part of the column which condense to a green liquid containing benzene and its homologues and some styrene, together with paraffins and *cyclo*hexanes, and resembling therefore, Caucasian petroleum.

The author suggests that in the interior of the earth alkali and alkali-earth metals are produced, together with their carbides. The action of water on these substances respectively produces hydrogen and acetylene, and these, in contact with finely divided nickel, cobalt, iron, &c., produce hydrocarbons in a manner similar to that described.

C. H. B.

Action of Nitric Acid on *iso*Pentane. By Petrus Poni (*Ann. sci. Univ. Jassy*, 1902, **1**, 53—58. Compare Abstr., 1900, i, 617).—The two solid substances previously obtained in this reaction are now shown to be respectively α-hydroxy*iso*butyric acid and a mixture (melting at 194—197°) of trinitro*iso*pentane and dinitro*iso*butane (compare Francis and Young, Trans., 1898, **73**, 928). The author regards the action as proceeding in the following way:

$$CHMe_2\cdot CH_2Me \rightarrow NO_2\cdot CMe_2\cdot CH(NO_2)\cdot CH_2\cdot NO_2 \rightarrow NO_2\cdot CMe_2\cdot CH_2\cdot NO_2 \rightarrow OH\cdot CMe_2\cdot CO_2H.$$

T. A. H.

New Reactions of Calcium Carbide and Acetylene. By O. Sandman (*Zeit. angew. Chem.*, 1902, **15**, 543—545).—A mixture of carbon tetrachloride and acetylene, when passed through a heated glass tube, reacts to form carbon and hydrogen chloride according to the equation $2C_2H_2 + CCl_4 = 5C + 4HCl$. Analogous results were obtained with carbon disulphide, chloroform, and bromoform, and also when any of these were passed over heated calcium carbide, the bye-products being calcium chloride, bromide or polysulphides, and hydrogen. The action of acetylene on potassium thiocyanate was investigated, the results confirming those of Conroy, Heslop, and Shores (Abstr., 1901, i, 373).

R. H. P.

Polymerism and Desmotropism of Trimethylethylene Nitrosite. By Julius Schmidt (*Ber.*, 1902, **35**, 2323—2335. Compare Abstr., 1901, i, 266; this vol., i, 21).—*β-Methyl-β-butylene* (*trimethylethylene*) *βγ-nitrosite*, $O:N\cdot CHMe\cdot CMe_2\cdot O\cdot N:O$, obtained by passing the undried fumes from arsenious oxide and nitric acid into an ethereal solution of β-methyl-β-butylene, is a blue oil which decomposes when distilled or even on exposure to diffused light; it has a pungent odour and is insoluble in water, dissolving quite readily, however, in the ordinary organic solvents excepting light petroleum.

The oil gives Liebermann's reaction and at the ordinary temperature partially undergoes polymerisation into *bis-trimethylethylene nitrosite*, $(C_5H_{10}N_2O_3)_2$, a solid substance crystallising in white needles and melting at 75—76° to a blue liquid; it is only slightly soluble in ether, glacial acetic acid, or the alcohols, but dissolves more readily in acetone, ethyl acetate, benzene, or ethylene dibromide. The molecular complexity of the two compounds was determined cryoscopically in benzene and ethylene dibromide solutions. The conversion of the original nitrosite into its polymeride is a balanced reaction, $2C_5H_{10}N_2O_3 \rightleftarrows (C_5H_{10}N_2O_3)_2$, and the inverse change occurs on warming the latter compound either alone or in solution, the phenomenon being analogous to that exhibited by nitrogen peroxide $2NO_2 \rightleftarrows N_2O_4$.

The nitrosite is most readily obtained in a pure state by heating its crystalline polymeride; it neither reacts with phenylcarbimide nor gives a coloration with ferric chloride.

These two nitrosites are at first insoluble in cold solutions of the alkali hydroxides, but they gradually undergo an isomeric change and then dissolve to a yellow solution.

β-Methyl-β-butylene $\beta\gamma$-isonitrosite, $O{:}N{\cdot}O{\cdot}CMe_2{\cdot}CMe{:}N{\cdot}OH$, the product of this intramolecular rearrangement, is precipitated from the alkaline, reddish-yellow solution by dilute sulphuric acid; it is soluble in water or the ordinary organic solvents and crystallises from light petroleum in mossy aggregates of white leaflets melting and decomposing at 125—126°.

The oxime character of the substance is demonstrated by the production of hydroxylamine by acidic hydrolysis and by its interaction with benzoyl chloride or phenylcarbimide.

The *benzoyl* derivative, $O{:}N{\cdot}O{\cdot}CMe_2{\cdot}CMe{:}N{\cdot}OBz$, obtained by the Schotten-Baumann reaction, crystallises from alcohol in white needles and melts at 135—136°. The *phenylcarbamide* derivative,

$$O{:}N{\cdot}O{\cdot}CMe_2{\cdot}CMe{:}N{\cdot}O{\cdot}CO{\cdot}NHPh,$$

produced by mixing its generators in ethereal solution, crystallises from alcohol in white needles decomposing at 151—152°. G. T. M.

Polymerism of Trimethylethylene Nitrosate. By JULIUS SCHMIDT (*Ber.*, 1902, **35**, 2336—2342. Compare preceding abstract). —On passing the gas evolved from heated lead nitrate into a cold ethereal solution of β-methyl-β-butylene, a product is obtained consisting chiefly of oily *β-methyl-β-butylene $\beta\gamma$-nitrosate*,

$$NO_2{\cdot}O{\cdot}CMe_2{\cdot}CHMe{\cdot}N{:}O,$$

together with a small amount of solid *bis-β-methyl-β-butylene nitrosate*. The former of these compounds is a bluish-green oil, decomposing when distilled under reduced pressure and rapidly polymerising into the latter substance. This polymeride, which was first prepared by Guthrie and called "amylene nitrosate," crystallises in cubical crystals and melts at 98—99°. The molecular complexity of the compounds was determined cryoscopically in benzene. A solution of the polymeride begins to exhibit dissociation at 30°, the maximum effect being observed at 60°. At the latter temperature, the solutions of the polymeride in the organic solvents have an intense bluish-green colour, and a molecular weight determination in boiling acetone showed that the substance is present in the unimolecular condition. A cryoscopic determination in naphthalene gave a similar result.

Both the nitrosates give Liebermann's reaction, and the mononitrosate slowly undergoes an isomeric change in the presence of alkali hydroxides and dissolves to a reddish-yellow solution.

G. T. M.

Flashing Points of Monohydric Fatty Alcohols and their Aqueous Solutions. By P. N. Raikow (*Chem. Zeit.*, 1902, **26**, 436—439. Compare Abstr., 1899, i, 47).—The higher the boiling point of an anhydrous monohydric fatty alcohol, the higher its flashing point. On dilution with water, the flashing point rises, the proportional rise at first diminishing to a minimum, then rapidly increasing In the case of alcohols which are not completely miscible with water, the minimum rise lies between the flashing point of the saturated solution of water in alcohol and that of the saturated solution of alcohol in water.

tert.-Butyl alcohol forms an exception, in that on dilution from 50 to 25 per cent. of alcohol the flashing point falls and rises again on further dilution. G. Y.

Action of Methyl Alcohol on its Sodium Derivative. By Marcel Guerbet (*Bull. Soc. Chim.*, 1902, [iii], **27**, 584—585).—Methyl alcohol, when heated with its sodium derivative, does not behave like the other alcohols; at 200°, it remains unchanged, and at 230—240° it decomposes with the formation of gaseous products. A. F.

Isomerisation of Unsaturated Alcohols and Saturated Glycols. By Iwan L. Kondakoff (*Chem. Zeit.*, 1902, **26**, 469—470. Compare Lieben, this vol., i, 336).—The mechanism of the reactions proposed by Lieben is identical with that previously suggested of the author (*J. pr. Chem.*, 1899, **60**, 264). G. Y.

Formation of Cuprous Xanthate. By Einar Biilmann (*Ber.*, 1902, **35**, 2184—2187).—The interaction of copper sulphate and potassium xanthate gives cuprous xanthate and ethyl dioxythiocarbonate, $S_2(CS{\cdot}OEt)_2$, which can be extracted from the yellow precipitate by ether. The decomposition is thus similar to that of sodium thiosulphate by copper sulphate, which gives sodium cuprous thiosulphate and sodium tetrathionate. W. A. D.

Synthesis of Carboxylic Acids. By Joseph Houben and Ludwig Kesselkaul (*Ber.*, 1902, **35**, 2519—2523).—Details are given of the syntheses of acetic, propionic, benzoic, and phenylacetic acids by passing carbon dioxide into an ethereal solution of the alkyl iodide, which has been treated with metallic magnesium. The yields amounted to about 50 per cent. (except in the case of acetic acid).

R. H. P.

Compound of Acetic Acid with Nitric Acid. By Amé Pictet and Paul Genequand (*Ber.*, 1902, **35**, 2526—2529).—Nitric acid of sp. gr. 1·4 reacts vigorously with an equal volume of acetic anhydride with the formation of *diacetylorthonitric acid*, $N(OAc)_2(OH)_3$, which is a colourless, fuming liquid boiling at 127·7° (corr.) under 730 mm. or at 45° under 17 mm. pressure. It has a sp. gr. 1·197 at 15° and 1·189 at 23°, and n_D 1·38432 at 23°; it is decomposed by water with development of heat and does not form stable salts.

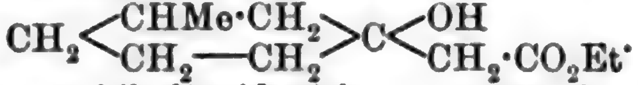
The analogous *dipropionylorthonitric acid* boils at 140—141° under 731 mm. or at 53—54° under 17 mm. pressure and has a sp. gr. 1·114 at 16°.

Attempts to prepare the corresponding formyl, *n*-butyryl, and *iso*valeryl compounds were not successful. R. H. P.

Reduction of Vinylacrylic Acid. By Johannes Thiele and Paul Jehl (*Ber.*, 1902, **35**, 2320—2321).—When vinylacrylic acid is reduced with sodium amalgam at 0° and the solution is prevented from becoming caustic by the passage of a current of carbon dioxide through it, βγ-pentenoic acid and not allylacetic acid (Doebner, this vol., i, 340) is formed; it was identified by its boiling point (191—195°) and by its dibromide (m. p. 65°). Doebner's product initially contained some allylacetic acid, produced by the transformation of the βγ-unsaturated acid into αβ-unsaturated acid by the sodium hydroxide formed from the amalgam, but this underwent reduction to valeric acid, so that finally a mixture of valeric acid and βγ-pentenoic acid was obtained. W. A. D.

Application of Sodamide as a Condensing Agent. By Martin Freund and Edmund Speyer (*Ber.*, 1902, **35**, 2321—2322).—Ethyl acetoacetate can be prepared by adding finely powdered sodamide to ethyl acetate. Similarly, although acetone is only slowly converted into *iso*phorone by the action of sodium ethoxide, it is immediately acted on by sodamide; the principal product is *iso*phorone, but it is accompanied by mesityl oxide, xylitone, and a viscid substance boiling at 190—215° under 16 mm. pressure. W. A. D.

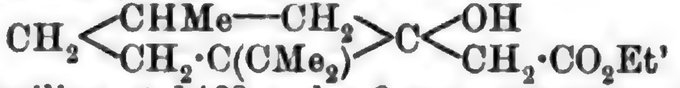
Condensations with Zinc and Ethyl Iodoacetate. By Léon Tétry (*Bull. Soc. Chim.*, 1902, [iii], **27**, 598—603).—If ethyl iodoacetate is allowed to act on 2-methyl*cyclo*hexanone in presence of zinc dust, and the resulting product then treated with water, there is formed *ethyl 1-methyl*cyclo*hexane-3-ol-3-acetate*,



$$\mathrm{CH_2}\!<\!\begin{matrix}\mathrm{CHMe{\cdot}CH_2}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{OH}\\ \mathrm{CH_2{\cdot}CO_2Et}\end{matrix}$$

It is a colourless, mobile liquid with an agreeable odour, which boils at 119—120° under 9 mm. pressure. When boiled with a solution of zinc chloride in glacial acetic acid, it loses water and forms *ethyl 1-methyl*cyclo-*Δ³-hexene-3-acetate*. On saponification with an alcoholic solution of potassium hydroxide, this ester yields the corresponding *1-methyl*cyclo-*Δ³-hexene-3-acetic* acid, which forms a colourless oil boiling at 146° under 18 mm. pressure; it has an acid reaction and gives a crystalline salt with copper.

In a similar manner, by the action of ethyl iodoacetate on pulegone, there is obtained *ethyl pulegolacetate*,



$$CH_2<\begin{matrix}CHMe—CH_2\\CH_2\cdot C(CMe_2)\end{matrix}>C<\begin{matrix}OH\\CH_2\cdot CO_2Et\end{matrix}$$

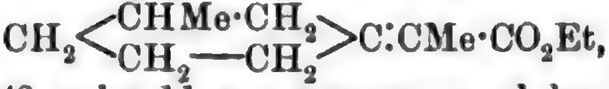
a colourless oil boiling at 142° under 9 mm. pressure. The yield is in this case very poor.

By the condensation of ethyl iodoacetate with citraldehyde, a mixture of substances is apparently obtained, from which, however, ethyl citralideneacetate, $C_9H_{15}\cdot CH\colon CH\cdot CO_2Et$, can be isolated as a colourless oil with an agreeable odour, which boils at 129° under 9 mm. pressure. From the products of reaction there was also isolated the *lactone*, $C_{14}H_{20}O_3$, which forms a colourless oil boiling at 160° under 10 mm. pressure. On saponifying ethyl citralideneacetate with an alcoholic solution of potassium hydroxide, the corresponding acid is obtained; it is a colourless, mobile oil which boils at 175° under 18 mm. pressure, has an acid reaction, and yields a crystalline copper salt. A. F.

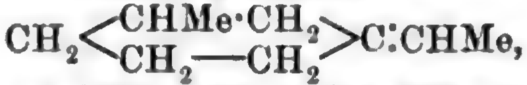
Replacement of Zinc by Magnesium in Certain Synthetical Reactions. By Nicolai Zelinsky and Johannes Gutt (*Ber.*, 1902, **35**, 2140—2144. Compare Abstr., 1901, i, 661).—Magnesium may with advantage be employed instead of zinc in promoting the condensation of aldehydes or ketones with the esters of the halogen substituted aliphatic acids.

Ethyl 1-methyl*cyclo*hexane-3-ol-3-acetate results from the condensation of 1-methyl*cyclo*hexane-3-one, and ethyl 1-methyl*cyclo*hexane-3-ol-3-propionate is readily obtained from ethyl α-bromopropionate, 1-methyl*cyclo*hexanone, and magnesium; the yield in this case is 30 per cent. of the theoretical, and by employing the corresponding α-iodo-ester, it may be raised to 45 per cent. When zinc is used as the condensing agent, only a small amount of the required ester is produced.

The *intermediate product*, $2MgBr\cdot O\cdot C_7H_{12}\cdot CHMe\cdot CO_2Et,Et_2O$, is a crystalline substance soluble in benzene, but not in light petroleum.



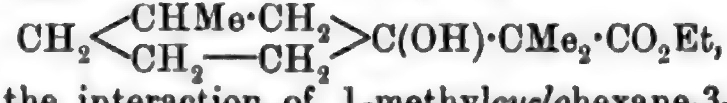
By digesting the preceding substituted propionate with crystallised oxalic acid, an unsaturated *ester*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C\colon CMe\cdot CO_2Et$, is obtained, which boils at 103—104° under 11 mm. pressure, and has a sp. gr. 0·9487 and n_D 1·4606 at 16°, and $[\alpha]_D$ +48·41°. Prolonged treatment with oxalic acid leads to further change, resulting in the production of the unsaturated *hydrocarbon*,



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C\colon CHMe,$$

a compound boiling at 150—151° under 738 mm. pressure; it has a sp. gr. 0·8154, and n_D 1·4538 at 19°, and $[\alpha]_D$ +56·63°.

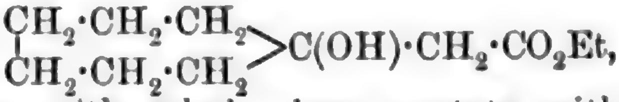
*Ethyl 1-methyl*cyclo*hexane-3-olisobutyrate*,



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C(OH)\cdot CMe_2\cdot CO_2Et,$$

obtained by the interaction of 1-methyl*cyclo*hexane-3-one and ethyl α-bromo*iso*butyrate in the presence of magnesium, boils at 131—132° under 13 mm. pressure; it has a sp. gr. 1·000 and n_D 1·4626 at 18°, and $[\alpha]_D$ +0·24°; this substance could not be isolated in a pure state by the use of zinc.

The unsaturated *ester*, $CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH\end{matrix}>C\cdot CMe_2\cdot CO_2Et$, results from the action of crystallised oxalic acid on the preceding compound; it boils at 110—112° under 11 mm. pressure, has a sp. gr. 0·9460 and n_D 1·4619 at 18°, and $[\alpha]_D$ +45·59°.

Ethyl cyclo*heptane*-1-*olacetate*,  $\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\|\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CO_2Et$, produced by condensing suberone with ethyl α-bromoacetate with magnesium suspended in absolute ether, boils at 133—134° under 11 mm. pressure; it has a sp. gr. 1·0392 and n_D 1·4686 at 17° (compare also this vol., i, 370 and 341). G. T. M.

Alkali Cobaltioxalates. By COPAUX (*Compt. rend.*, 1902, **134**, 1214—1216).—By dissolving cobaltous oxalate in a solution of the alkali oxalate, and adding the calculated quantity of lead peroxide and some acetic acid, the author has prepared the following cobaltioxalates, $(NH_4)_6Co_2(C_2O_4)_6,6H_2O$ (monoclinic), $K_6Co_2(C_2O_4)_6,7H_2O$ (triclinic), $Rb_6Co_2(C_2O_4)_6,8H_2O$ (rhombic), $Na_6Co_2(C_2O_4)_6,10H_2O$ (monoclinic), $Li_6Co_2(C_2O_4)_6,12H_2O$ (triclinic), $K_5Na_{19}Co_8(C_2O_4)_{24},32H_2O$ (pseudo-cubic), $Na_3Rb_3Co_2(C_2O_4)_6,5H_2O$ (monoclinic),

$$Na_3(NH_4)_3Co_2(C_2O_4)_6,7H_2O$$

(monoclinic). These salts are green, opaque, and dichroic; they dissolve in water, but dilute solutions decompose gradually at the ordinary temperature, and immediately on boiling, with precipitation of cobaltous oxalate. The solutions give no precipitate with calcium chloride, but are immediately, although partially, decomposed by alkali hydroxides. The ammonium, potassium, and rubidium salts are not isomorphous as in the iron, chromium, aluminium series. C. H. B.

Niobioxalic Acid. By FRANZ RUSS (*Zeit. anorg. Chem.*, 1902, **31**, 42—91).—The author gives an historical account of the complex metallo-oxalates which have been prepared, and as a criterion of the complexity he takes the stability of the ammonium compounds in water.

The niobic acid used in the investigation was extracted from Norwegian columbite by a modified form of Marignac's method. By fusing niobic acid with potassium carbonate and dissolving the residue in water, then adding oxalic acid and evaporating, a solid substance separates out which can be represented by the formula

$$Nb_2O_5,3K_2O,6C_2O_3,4H_2O;$$

it can be recrystallised from water. Attempts to prepare other potassium niobioxalates were fruitless. The corresponding sodium salt, $Nb_2O_5,3Na_2O,6C_2O_3,8H_2O$, was prepared in a similar manner. It forms supersaturated solutions much more easily than the potassium salt. The ammonium salt, $Nb_2O_5,3(NH_4)_2O,6C_2O_3,3H_2O$, was obtained by fusing niobic oxide with potassium carbonate and decomposing the niobate with hydrochloric acid; the hydrated niobic acid was then dissolved in a solution of ammonium binoxalate. From the solution, large crystals of the ammonium salt separate on cooling, and it can be completely precipitated by the addition of acetone. The rubidium salt, $Nb_2O_5,3Rb_2O,6C_2O_3,4H_2O$, which is very easily soluble in water, was prepared in the same way as the potassium salt.

From a solution of niobic acid containing excess of oxalic acid there crystallises a niobioxalic acid of the formula $Nb(C_2O_4H)_5$, which, however, is decomposed by water. By treatment with alcohol, a residue of the unstable compound, $Nb_2O_5,C_2O_3,4H_2O$, has also been obtained.

A solution of potassium niobioxalate gives precipitates with solutions of barium, strontium, and calcium salts; the precipitated barium salt has the formula $Nb_2O_5,5BaO,10C_2O_3,20H_2O$. The following ions also give precipitates: $Fe^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$, $UO_2^{\cdot}$, $Ag^{\cdot}$, $Hg^{\cdot}$, and $Pb^{\cdot\cdot}$, whilst $Mn^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, and $Hg^{\cdot\cdot}$ do not. When heated in a current of chlorine, carbon tetrachloride, or hydrogen chloride, potassium niobioxalate leaves a residue of potassium chloride and niobic oxide. When heated in a current of carbon disulphide, a residue is left which contains carbon, a potassium polysulphide, and a niobium compound containing sulphur, but of composition varying with the conditions of the experiment.

From the results of conductivity measurements with polished platinum electrodes (platinised electrodes cause a catalytic decomposition), it is deduced that the salts are hydrolysed in aqueous solution.

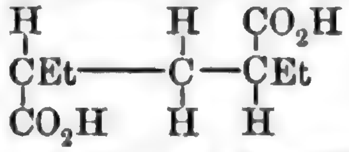
No positive result was obtained in an attempt to effect the separation of niobium and tantalum by means of the complex oxalates.

J. McC.

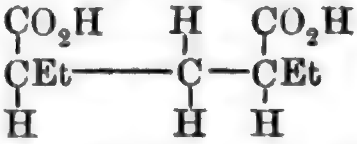
Complex Salts of Osmium: Potassium Osmyloxalate. By Maurice Vèzes and L. Wintrebert (*Bull. Soc. Chim.*, 1902, [iii], 27, 569—578).—If osmium peroxide, dissolved in an aqueous solution of pure potassium hydroxide, is treated with excess of oxalic acid, and the solution thus obtained heated to boiling in a flask fitted with an upright condenser until vapours of peroxide cease to be disengaged (several hours), a crystalline deposit of potassium osmyloxalate separates from the liquid on cooling. The yield is practically quantitative. The same compound is also formed by adding excess of oxalic acid to a hot concentrated solution of potassium oxalate, or by digesting osmium peroxide with a concentrated solution of potassium dioxalate in the cold. This salt, which has the formula $K_2OsO_2(C_2O_4)_2,2H_2O$, forms triclinic crystals showing dichroism (yellowish-green and brownish-yellow); in the dry state, the crystals are comparatively stable, but on heating at 80° lose their water of crystallisation. On heating more strongly, decomposition occurs, carbon dioxide is evolved, and a mixture of osmium protoxide and potassium carbonate is left. Potassium osmyloxalate is very sparingly soluble in cold water, but the solubility increases with rise of temperature; it is almost insoluble in a solution of potassium chloride. In aqueous solution in the cold, more quickly on heating, potassium osmyloxalate slowly decomposes with formation of osmic acid; this decomposition is prevented by the presence of a small quantity of potassium oxalate, oxalic acid, or hydrogen potassium oxalate. When treated with ammonia, a yellow, crystalline precipitate of osmyldiammonium oxalate (Abstr., 1882, 144) is produced, and on being treated with hydrochloric acid chlorine is evolved and potassium chloro-osmate formed. A. F.

s-aa-Diethylglutaric Acid and its Preparation from the Corresponding *β*-Hydroxy-acid.

By Sergius N. Reformatsky (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 357—370).—Two symmetrical *aa*-diethylglutaric acids were prepared by Auwers (Abstr., 1896, i, 639), one melting at 118—119° and the other at 76—78°, but the individuality of the latter was not established. The first of these acids has been obtained in large quantity by the author by preparing the corresponding *β*-hydroxy-acid and acting on this with hydriodic acid. It is found that the acid obtained in this way melts at 119·5—120°, and when treated with nitric acid is partially converted into a stereoisomeric modification melting at 93·5—94·5°. The latter is shown to be the fumaric form of *s-aa*-diethylglutaric acid having the structure I, whilst the other, melting at 119·5—120°, which readily forms an anhydride, is the maleic modification of the constitution II:

I. 

$$\begin{array}{ccccc} H & & H & & CO_2H \\ | & & | & & | \\ CEt & — & C & — & CEt \\ | & & | & & | \\ CO_2H & & H & & H \end{array}$$

II. 

$$\begin{array}{ccccc} CO_2H & & H & & CO_2H \\ | & & | & & | \\ CEt & — & C & — & CEt \\ | & & | & & | \\ H & & H & & H \end{array}.$$

The acid melting at 76—78°, described by Auwers (*loc. cit.*), consists of a mixture of the two above stereoisomerides.

s-*Ethyl β-hydroxy-aa-diethylglutarate*, $\mathrm{OH{\cdot}CH(CHEt{\cdot}CO_2Et)_2}$, obtained by the action of zinc on a mixture of ethyl formate and ethyl *a*-bromobutyrate, is a colourless liquid which boils at 283—284° and readily dissolves in alcohol or ether; it has the normal molecular weight in boiling ether, a sp. gr. of 1·01682 at 20°/4°, 1·01018 at 22·4°/4°, 1·00899 at 24·3°/4°, and 1·00675 at 25·9°/4°; n_D at 20°, 1·4405. The corresponding acid was obtained as a pale yellow syrup, soluble in water, alcohol, or ether. The *barium* salt, with $2H_2O$, was prepared and analysed.

The maleic form of *aa*-diethylglutaric acid crystallises from water in large, shining, monoclinic prisms [$a : b = 1·261 : 1$; $\beta = 76°7'$].

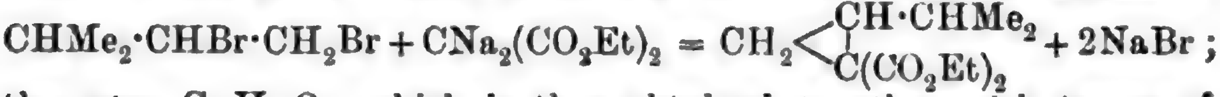
The fumaric modification, melting at 93·5—94·5°, separates from aqueous solution in monoclinic crystals, which are more readily soluble in water than those of the stereoisomeride; [$a : b : c = 0·8848 : 1 : 2·2743$; $\beta = 75°20'$]. The *potassium* salt was prepared and analysed.

The relations between the three *s-aa*-diethylglutaric acids, melting at 119·5—120°, 93·5—94·5°, and 76—78° respectively, are thus similar to those existing in the case of the corresponding dimethyl acids melting at 140—141°, 127—128°, and 102—104°; with the latter acids, however, the maleic modification has a lower melting point than the fumaric form. T. H. P.

Action of Ethyl Sodiomalonate on the Dibromides $C_nH_{2n}Br_2$. III.

By Wladimir Ipatieff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 351—356. Compare Abstr., 1899, i, 481 and 673).—The action of ethyl sodiomalonate on *aγ*-dibromo-*β*-dimethylpropane gives rise to a crystalline *ester* melting at 105—105·5°; the corresponding *acid*, $C_7H_8O_4$, decolorises potassium permanganate and gives a *bromo*-derivative melting at 127—128°. The structure of the acid has not yet been ascertained.

The interaction of ethyl sodiomalonate and αβ-dibromo-γ-methylbutane takes place mainly according to the following equation:

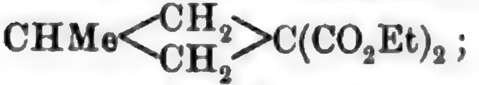


$$CHMe_2\cdot CHBr\cdot CH_2Br + CNa_2(CO_2Et)_2 = CH_2<\begin{array}{l}CH\cdot CHMe_2\\ |\\ C(CO_2Et)_2\end{array} + 2NaBr;$$

the *ester*, $C_{12}H_{20}O_4$, which is thus obtained, together with traces of ethyl ethanetetracarboxylate, boils at 122—132° under 18 mm. pressure, and the corresponding iso*propyltrimethylenedicarboxylic acid* separates from chloroform in crystals melting at 76—78° and is soluble in water, benzene, or ether; it does not decolorise permanganate solution or combine directly with bromine, and when heated at its melting point it loses carbon dioxide, giving *iso*propyltrimethylenecarboxylic acid; its *potassium, calcium*, and *silver* salts were prepared.

[With S. BORDELIUS.]—The action of ethyl sodiomalonate on ψ-butylene dibromide yields bromobutylene, CHMe:CBrMe, and a small quantity of ethyl ethanetetracarboxylate. With *iso*butylene dibromide, ethyl sodiomalonate gives *iso*butylene, bromo*iso*butylene, CMe_2:CHBr, and ethyl ethanetetracarboxylate.

[With W. MICHAELADZE.]—The action of ethyl sodiomalonate on αγ-dibromobutane gives traces of a bromo-compound together with *diethyl methyltetramethylenedicarboxylate*, which is formed according to the equation:



$$CHMeBr\cdot CH_2\cdot CH_2Br + CNa_2(CO_2Et)_2 = 2NaBr + CHMe<\begin{array}{l}CH_2\\ CH_2\end{array}>C(CO_2Et)_2;$$

this ester boils at 155—165° under 15 mm. pressure, and the corresponding *acid*, $C_7H_{10}O_4$, separates from chloroform in crystals, which melt at 157—158° and are soluble in water, alcohol, ether, or benzene; the *potassium, ammonium, calcium*, and *silver* salts were prepared.

The author draws the following conclusions concerning the course followed by the reaction between ethyl sodiomalonate and dibromides: (1) Dibromides in which the bromine atoms are attached to neighbouring carbon atoms only yield closed-chain trimethylene acids when the carbon atoms to which the bromine atoms are joined are either both primary or one primary and the other secondary. (2) Dibromides in which the bromine atoms are combined either with two secondary, or with one primary and one tertiary, carbon atoms give no acid, but mostly an unsaturated bromide; when the carbon atoms in question are secondary and tertiary respectively, there are formed, besides an unsaturated bromide, a hydrocarbon of the ethylene series and ethyl ethanetetracarboxylate. (3) Dibromides in which the bromine atoms are joined to two carbon atoms separated by another carbon atom yield closed-chain tetramethylene acids in cases where these carbon atoms are either both primary or one primary and the other secondary; if one of the carbon atoms is tertiary, the reaction gives an unsaturated substituted *gem.*-allylmalonic acid. T. H. P.

Camphoric Acid. XI. Confirmation of Bredt's Formula; some Derivatives of Inactive Camphoric Acid. By WILLIAM A. NOYES and AUSTIN M. PATTERSON (*Amer. Chem. J.*, 1902, **27**, 425—433).—Dihydro-α-campholytic acid (Abstr., 1901, i, 664) has been carried through the same series of transformations as dihydro-β-campholytic acid (Abstr., 1899, i, 284), namely, conversion into bromo-derivative, saponification into hydroxy-compound, elimination of carbon dioxide, and finally, formation of oxime. The *oxime* is that of 2 : 2 : 3-*trimethyl*cyclo*pentanone*, and it crystallises in plates which melt at 104°. It is shown that this result, in conjunction with that previously obtained, can only be explained by Bredt's formula. Some reactions of α-campholytic acid are pointed out which cannot readily be explained by current stereochemical theories.

From a specimen of artificially prepared inactive camphor (m. p. 176°) *β-camphoramidic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH_2$, has been prepared by passing ammonia through an alcoholic solution and treating the resulting product with sodium hydroxide; it crystallises in needles which melt at 178°.

i-*Aminodihydrocampholytic acid*, $NH_2\cdot C_8H_{14}\cdot CO_2H$, prepared by the method adopted for the active isomeride (Abstr., 1895, i, 187), crystallises in leaflets which closely resemble the active modification. The *anhydride* melts at 188°.

When treated with 0·5 mol. of sulphuric acid and 1 mol. of sodium nitrite, the amino-acid decomposes and gives i-*dihydrocampholytic acid* which melts at 173° and i-*α-campholytic acid* which was obtained as a liquid. J. McC.

Preparation of Malic Acid from Stems of Rhubarb. By NICOLA CASTORO (*Landw. Versuchs-Stat.*, 1902, **56**, 423—424).—The acid was separated as the strontium salt. This salt did not crystallise in nodules containing 1½ mols. H_2O as usually described, but in needles, or sometimes in plates, and contained $4H_2O$.

N. H. J. M.

Substitution of Hydrogen for Chlorine in Trichloromethylparaconic Acid. By HENRY C. MYERS (*J. Amer. Chem. Soc.*, 1902, **24**, 525—528).—The author has shown (Trans., 1897, **71**, 614) that when trichloromethylparaconic acid is reduced with zinc dust or sodium amalgam, dichloromethylparaconic acid is obtained. If, however, the reduction with sodium amalgam is continued for 7—10 days, the products consist of dichloromethylparaconic acid, chlorodiparaconic acid, and an *acid* which resembles benzoic acid in appearance and melts at 126—127°. When chlorodiparaconic acid is heated above its melting point, it suffers decomposition with elimination of a molecular proportion of hydrogen chloride. E. G.

The Degradation of Rhamnonic and *iso*Saccharic Acids. By OTTO RUFF (*Ber.*, 1902, **35**, 2360—2370).—[With HUGO KOHN.]—Calcium rhamnonate, $Ca(C_6H_{11}O_6)_2$, obtained as a white, stable salt by oxidising rhamnose with an aqueous suspension of bromine, and treating the product successively with lead carbonate, silver oxide, and calcium carbonate, is precipitated from the concentrated final mother liquor by adding alcohol. This salt, when treated with ferric acetate and hydrogen peroxide, is oxidised to methyltetrose, which is isolated in the form of its *phenylbenzylhydrazone* by adding an alcoholic solution of phenylbenzylhydrazine to the crude syrupy sugar dissolved in the same solvent. This hydrazone crystallises from benzene or alcohol in needles melting at 96—97°; it has $[\alpha]$ $-6.5°$ for white light.

Methyltetrose is produced by decomposing the preceding compound with 40 per cent. formaldehyde solution and obtained in the form of a syrup exhibiting multirotation. The freshly prepared solution has $[\alpha]_D$ $-30.5°$, this value diminishes and after 4 hours remains constant at $-16.35°$. When treated with sodium diazobenzenesulphonate, the sugar develops a violet coloration and is therefore an aldose; it yields an *ethyl-mercaptal*, $C_9H_{20}O_3S_2$, by condensation with ethyl mercaptan in the presence of concentrated hydrochloric acid; this derivative crystallises in white, tasteless, and odourless needles melting at 108—109°.

Methyltetronic acid, produced by oxidising methyltetrose with bromine, separates from aqueous solution in the form of its *lactone*, a substance crystallising in needles and having $[\alpha]_D$ $-47.5°$. All the metallic methyltetronates excepting the copper salt are amorphous, and the latter, although crystallising in needles, is unstable when heated on the water-bath. The *brucine* salt, however, crystallises well from absolute alcohol in needles melting at 145—150°; it is readily soluble in water but dissolves more sparingly in the ordinary organic solvents. Other alkaloids also yield well crystallised methyltetronates.

The *phenylhydrazide* crystallises from ethyl acetate in silky, snow-white leaflets and melts at 169° (corr.).

[With ADOLF MEUSSER and ARTHUR FRANZ.]—When treated in aqueous solution with hydrogen peroxide and ferric acetate, lead *iso*saccharate gives rise to a new ketose (*pentanetriolone*), which is obtained in the form of a syrup after evaporating the filtered mother liquors under diminished pressure. The ketose has $[\alpha]_D$ $-36°$ and does not develop a coloration with sodium diazobenzenesulphonate. The *osazone* crystallises from benzene in needles containing benzene of crystallisation; the latter is removed at 80°, and the compound melts at 125°; it is soluble in the ordinary organic solvents excepting petroleum and is optically inactive. The *phenylbenzylhydrazone*, $C_{18}H_{22}O_3N_2$, of the pentanetriolone, formed by heating its generators dissolved in dilute alcohol, crystallises from benzene or water in pale yellow needles, melting at 124—126° and decomposing at 200°; it is readily soluble in hot water or the ordinary organic solvents excepting light petroleum and is optically inactive. The ketose yields an uncrystallisable oxime, and on reduction with sodium amalgam gives rise to a mixture of the two pentaerythritols. G. T. M.

Synthesis of Aldehydes of the Acetic Series by means of Nitromethane. By LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1902, **134**, 1226—1228).—When the compounds $R\cdot CH(OH)\cdot CH_2\cdot NO_2$, obtained by Henry by the condensation of aldehydes of the acetic series with nitromethane, are dehydrated by boiling their acetic acid solutions with zinc chloride, they yield nitrohydrocarbons of the type $R\cdot CH{:}CH\cdot NO_2$. When the latter are reduced with aluminium amalgam or with zinc and acetic acid, they yield oximes,

$$R\cdot CH_2\cdot CH{:}N\cdot OH.$$

The product of the condensation of valeraldehyde and nitromethane described by Henry yields *nitroisohexylene*, $CHMe_2\cdot CH_2\cdot CH{:}CH\cdot NO_2$, when dehydrated; it is a pale yellow liquid which boils at 80—81° under 10 mm. pressure, volatilises in steam, has a very pungent odour, and a sp. gr. 0·995 at 0°/0°. When reduced, it yields iso*hexaldoxime*, a colourless liquid with a disagreeable odour which boils at 90—91° under 20 mm. pressure, has a sp. gr. 0·910 at 0°/0°, and when hydrolysed, yields *iso*hexaldehyde. Heptaldehyde and nitromethane yield a pale yellow liquid boiling at 138—140° under 10 mm. pressure with slight decomposition, and its dehydration product is *nitro-octylene*, $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot NO_2$, a pale yellow liquid which has a very disagreeable odour, boils at 113—115° under 8 mm. pressure, and has sp. gr. 0·970 at 0°/0°. When reduced, it yields *octaldoxime*, $CH_3\cdot[CH_2]_6\cdot CH{:}NOH$, which melts at 56°, boils at 120—125° under 10 mm. pressure, and yields octaldehyde when hydrolysed.

C. H. B.

Study of Methyl Nonyl Ketone, Methyl Heptyl Ketone, and their corresponding Secondary Alcohols. By C. MANNICH (*Ber.*, 1902, **35**, 2144—2146).—Methyl heptyl ketone and methyl nonyl ketone, both contained in oil of rue, are readily reduced, yielding the corresponding secondary alcohols.

Methylheptylcarbinol boils at 87·5° under 10 mm. pressure and at 193—194° under the ordinary pressure. Methylnonylcarbinol boils at 120° under 14 mm. pressure; its *acetyl* derivative boils at 147—149° under 42 mm., and the *benzoyl* derivative at 197·5—200° under 15 mm. pressure. The *phenylcarbamate* and the *oxalate* of the latter carbinol melt at 36·5—37° and 34·5° respectively.

When dehydrating agents act on these alcohols, Δ^{β}-olefine derivatives are formed, the removal of water taking place between the second and third carbon atoms of the chain.

Δ^{β}-*Undecylene*, $C_{11}H_{22}$, boils at 192—193° and yields a colourless, oily *dibromide*, $C_{11}H_{22}Br_2$, boiling at 145—146° under 9 mm. pressure; the latter substance on treatment with potassium hydroxide loses hydrogen bromide and gives rise to $\beta\gamma$-*undecinene*, $C_{11}H_{20}$, a colourless liquid boiling at 81·5° under 10 mm. and at 199—201° under the ordinary pressure; this hydrocarbon has an unpleasant odour.

Methylnonylcarbinol, when subjected to the action of dehydrating agents, gives rise to the *ether*, $(C_{11}H_{23})_2O$, a light yellow liquid boiling at 198—200° under 10 mm. pressure.

Undecylene dibromide, on treatment with silver acetate, yields *undecane*-$\beta\gamma$-*diol*, a compound separating in crystals having a greasy lustre and melting at 51—53°.

Δ^{β}-*Nonylene* boils at 147—148° under the ordinary pressure.

When reduced, the oximes of methyl nonyl ketone and methyl heptyl ketone yield the corresponding amines, β-*undecylamine* and β-*nonyl-*

amine, boiling respectively at 113—114° under 26 mm., and at 69—70° under 11 mm. pressure.

The *ketone*, $C_9H_{19}\cdot CMe\dot{:}CH\cdot CO\cdot C_9H_{19}$, is produced by saturating methyl nonyl ketone with hydrogen chloride and distilling the oily additive product, $C_{22}H_{43}OCl$, under diminished pressure; it boils at 214—216° under 10 mm. pressure, and although its phenylhydrazone and semicarbazone are oily, yet the *picrate* of its aminoguanidine compound is crystalline and melts at 125—126°. The unsaturated ketone is not affected by 10 per cent. sulphuric acid, but a stronger solution (60 per cent.) reconverts it into methyl nonyl ketone. G. T. M.

Behaviour of Diketones towards Organo-magnesium Compounds. By NICOLAI ZELINSKY (*Ber.*, 1902, **35**, 2138—2140).—Diacetyl, when mixed with a cold suspension of magnesium methiodide in absolute ether, is readily converted into pinacone, the product being characterised by its boiling point (171—173°), and the crystalline hydrate melting at 46°.

Acetylacetone and the organo-magnesium compound interact energetically, but the yield of product is only small and consists of a glycol corresponding in composition with the formula $C_7H_{16}O_2$, and boiling at 100—102° under 16 mm. pressure.

Acetonylacetone, when similarly treated, gives a quantitative yield of *βε-dimethylhexane-βε-diol*, $OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH$, a glycol soluble in the ordinary organic solvents and crystallising in long prisms melting at 92—93°; these crystals, when separating from benzene or toluene, exhibit a greenish-violet fluorescence while remaining in contact with the mother liquor.

The dibromide, $C_8H_{16}Br_2$, obtained by the action of a glacial acetic acid solution of hydrogen bromide on the glycol, crystallises from light petroleum in prisms melting at 71—72°. G. T. M.

Behaviour of Araban with Fehling's Solution. By ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1902, **35**, 240—245. Compare Salkowski, this vol., i, 206).—The author finds that his previous statement, that araban in alkaline solution is not precipitated by Fehling's solution, is inaccurate. A solution in dilute sodium hydroxide, containing 8 per cent. of this substance prepared from gum arabic, is precipitated on addition of one-fifth of its volume of Fehling's solution, but if the amount of the latter be increased to one-third, only a slight precipitate is formed, whilst with equal volumes of the two liquids a clear mixture is produced, the precipitate being soluble in excess of the reagent. The corresponding xylan precipitate does not appear to be soluble in excess. The author's previous experiments were carried out with araban obtained from beet-root, which was not precipitated by addition of about one-third of its volume of Fehling's solution, whence he concludes either that this araban is not identical with that contained in gum arabic, or that it had undergone some change during preparation. The latter supposition is, he considers, the more probable, although it is not in accordance with the fact that araban, prepared by the same process from gum arabic, undergoes no change.

T. A. H.

Crystallised Stachyose. By ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1902, **56**, 419—423. Compare *ibid.*, **40**, 218).—By slightly modifying the process previously employed, stachyose was obtained in large, colourless, lustrous plates, probably triclinic. The crystals only contain traces of mineral matters. The composition of the crystals corresponds with the formula $C_{18}H_{32}O_{16},3H_2O$.

Stachyose containing water of crystallisation gives $[\alpha]_D$ +133·5°; nearly the same number (+135°) is obtained with a 10 per cent. aqueous solution of uncrystallised air-dried stachyose at 16°.

N. H. J. M.

Behaviour of Silver Haloids with Organic Amino-bases. By BERTHOLD WUTH (*Ber.*, 1902, **35**, 2415—2420).—The solubility of silver chloride and bromide in aqueous methylamine or ethylamine has been determined (compare Bodländer and Fittig, this vol., ii, 248). In both cases, the solubility increases with increase of the concentration of the base, but when the results are expressed on a system of ordinates, the solubility curve in methylamine is concave to the abscissa, whereas that in ethylamine is convex to that axis. It appears most probable that in methylamine the complexes $3AgCl,NH_2Me$ and $3AgBr,NH_2Me$ are present.

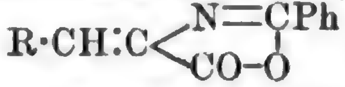
The double *salt*, $AgBr(C_5NH_5,HBr)_2$, is prepared by adding the double salt of silver chloride and pyridine hydrochloride to a boiling concentrated solution of potassium bromide; it forms a white, crystalline powder which is decomposed by water. The corresponding double *iodide* crystallises in needles. Silver and piperidine form a double *chloride*, $AgCl(C_5NH_{11},HCl)_3$, and a double *bromide* which crystallises from chloroform in white leaflets, and a double *iodide* which crystallises in needles (compare Renz, this vol., i, 563). K. J. P. O.

Transformation of Glyoxylic Acid into Glycine by the Action of Ammonia. By EMIL ERLENMEYER and JULIUS KUNLIN (*Ber.*, 1902, **35**, 2438—2440).—Just as phenylpyruvic acid reacts with ammonia yielding phenylacetylphenylalanine (α-phenylacetylamino-β-phenylpropionic acid) (Abstr., 1899, i, 761), and pyruvic acid and ammonia give α-acetylaminopropionic acid with elimination of water and carbon dioxide (de Jong, Abstr., 1901, i, 130), so do glyoxylic acid and ammonia produce formylaminoacetic acid when heated together at 100°. Formylaminoacetic acid was not isolated from the oily product of the reaction, but on hydrolysing with hydrochloric acid, formic acid and glycine were isolated; the latter was obtained as the copper salt, and by interaction with benzaldehyde and acetic anhydride was converted into the azlactone (see next page). K. J. P. O.

Amino-acids of the $C_nH_{2n+1}O_2N$ Series. By FRIEDRICH KUTSCHER (*Sitzungsber. K. Akad. Wiss. Berlin.*, 1902, 588—592).—To prepare the silver salts of the amino-acids of this series, a solution of silver nitrate is added in very slight excess to an aqueous solution of the acid, then a cold saturated solution of barium hydroxide is added with continual shaking. Silver oxide is at first precipitated, then redissolves, and the silver salt separates in a crystalline form.

In this way, the silver salts of glycine, aminovaleric acid, and leucine have been obtained; it has not been possible to prepare the salts of *a*-alanine or sarcosine. The method may possibly be useful for separating the decomposition products of albumin. J. McC.

Amino-acids prepared from Plants. By Ernst Schulze and Ernst Winterstein (*Zeit. physiol. Chem.*, 1902, **35**, 299—314).—Methods for the preparation of amino-acids from plants are described, and several of the more common substances of this class have been re-examined, and especially their specific rotations and solubilities re-determined, with results generally in accordance with those of previous observers. The authors show that the aminovaleric acid occurring in *Lupinus* species is identical with that obtained by E. Fischer (Abstr., 1901, i, 780) as a hydrolytic product of casein, and that the seedlings of *Vicia sativa* contain, in addition to leucine, an isomeride of the latter differing from it by having a higher specific rotation. T. A. H.

Azlactones and the Conversion of Pyroracemic Acid into Methylpyruvic Acid. By Emil Erlenmeyer, jun. (*Ber.*, 1902, **35**, 2483—2486. Compare Abstr., 1900, i, 549).—The compounds formed by the condensation of aldehydes with hippuric acid have probably the formula  $R{\cdot}CH{:}C{<}\begin{matrix}N{=}CPh\\ CO{-}O\end{matrix}$, and the author therefore terms them *azlactones*, from analogy with the unsaturated $\beta\gamma$-lactones formed from γ-ketonic acids. This constitution is confirmed by the behaviour of the condensation product of pyruvic acid with hippuric acid, which was first described by Hoffmann (*Ber.*, 1886, **19**, 2554). This substance dissolves in aqueous sodium carbonate, a salt of the formula $CO_2Na{\cdot}CMe{:}C(CO_2Na){\cdot}NH{\cdot}COPh$ being formed; when the solution is acidified in the cold, no precipitate is formed, the corresponding dibasic acid being soluble, but when the liquid is heated, the β-azlactone is at once re-formed and precipitated. When the azlactonecarboxylic acid is heated for some time with hydrochloric acid, it is completely hydrolysed, yielding benzoic acid and methylpyruvic acid, formed from the benzamide and methyloxaloacetic acid, which are the primary products. This reaction affords a method for passing from an *a*-ketonic acid to the next higher homologous acid. Phenylpyruvic acid, however, and certain of its derivatives do not appear to undergo this reaction, which is being applied to other acids of the same type. A. H.

Dithiocarbamic Esters derived from Primary Amines. By Marcel Delépine (*Compt. rend.*, 1902, **134**, 1221—1223).—The preparation of esters of the dithiourethanes of the general formula $RNH{\cdot}CS{\cdot}SR'$ is simplified by allowing 1 mol. proportion of a haloid ester to act on the thiocarbonic derivatives of the primary amines $NHR{\cdot}CS{\cdot}S{\cdot}NH_3R + XR' = NHR{\cdot}CS{\cdot}SR' + X{\cdot}NH_3R$. In the case of amines such as those of the benzene series, which are only slightly basic, it is better to adopt the Losanitsch's method and allow the amine to act on a mixture of carbon disulphide and ammonia, yielding a compound, $RNH{\cdot}CS{\cdot}SNH_4$, which is readily acted on by the haloid ester. This method is also applicable to secondary amines, yielding compounds such as $NMePh{\cdot}CS_2{\cdot}NH_4$, $NEtPh{\cdot}CS_2{\cdot}NH_4$, from which the dithiourethanes are readily obtained.

The author has prepared a number of mono-substituted dithiourethanes, and confirms Hoffmann's statement that when heated they readily split up into a thiocarbimide and mercaptan. With a further mol. proportion of haloid ester, they yield compounds such as $NMe{:}C(SMe){\cdot}SEt$ and $NMe{:}C(SMe){\cdot}S{\cdot}CH_2Ph$. With ammonia and substituted ammonias, the reaction $R{\cdot}NH{\cdot}CS{\cdot}SR' + NHR''R''' = R{\cdot}NH{\cdot}CS{\cdot}NR''R''' + HS{\cdot}R'$ takes place almost quantitatively. Powerful oxidation yields results similar to those obtained with di-substituted dithiourethanes. With weak oxidising agents, the result depends on whether the radicle attached to the nitrogen is alkylic or aromatic; for example, $NHMe{\cdot}CS{\cdot}S{\cdot}CH_2Ph$ is not attacked, whilst $C_6H_4Me{\cdot}NH{\cdot}CS{\cdot}SMe$ yields $S_2[C(SMe){:}N{\cdot}C_6H_4Me]_2$. The author concludes that the compounds derived from alkylamines have the constitution $R{\cdot}NH{\cdot}CS{\cdot}SR'$, whilst those derived from aromatic amines have the constitution $R{\cdot}N{:}C(SH){\cdot}SR'$, the constitution being determined by the more or less acid character of the radicle R. Potassium hydroxide in dilute alcohol dissolves the second but not the first; nitrous acid yields nitroso-derivatives with the first, but simply oxidises the second. C. H. B.

New Properties of Urea. By WILLIAM RAMSDEN (*Proc. Physiol. Soc.*, 1902; *J. Physiol.*, **28**, xxiii—xxvi).—The presence of urea dissolved to saturation prevents the heat coagulation of proteids. Various proteids, including gelatin, swell up and dissolve in saturated solutions; the substances formed are acid-albuminate and alkali-albuminate, according to the original reaction of the solution. Urea, up to 10 per cent., increases proteolytic digestion; beyond this strength, it has a retarding influence. Urea is valuable in histology, its action on connective tissues facilitating the separation of a tissue into its individual elements. Urea forms crystalline compounds with fatty acids. Ammonium cyanate and thiocyanate produce many of the effects of urea. Ammonia and ammonium carbonate do not. W. D. H.

Some Cases of the Wandering of Oxygen in the Molecule. By O. LUTZ (*Ber.*, 1902, **35**, 2460—2466).—When *l*-bromosuccinic acid is treated with aqueous or methyl alcoholic ammonia (compare Abstr., 1898, i, 127), the ammonium salt of *d*-β-malamic acid, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, is formed, the bromine atom being replaced by a hydroxyl group; the acid crystallises in monoclinic plates melting at 149°, has a sp. gr. 1·577 at 18°/4°, and $[\alpha]_D$ $+9{\cdot}70°$; the *silver* salt crystallises in leaflets. *l*-β-Malamic acid is similarly obtained from *d*-chlorosuccinic acid; it melts at 149°, has a sp. gr. 1·576 at 18°/4°, and $[\alpha]_D$ $-9{\cdot}33°$; the sodium salt has $[\alpha]_D$ $-27{\cdot}32°$; each acid is easily converted into the corresponding malic acid by boiling with alkalis. *r*-β-Malamic acid was prepared from *r*-bromosuccinic acid; it melts at 148°, has a sp. gr. 1·526 at 18°/4°, and is less soluble in water than the active acids. Using Curtius and Koch's method (Abstr., 1889, i, 376), *r*-β-malamic acid was obtained from aspartic acid and not α-malamic acid, as these authors supposed.

l-β-Malamic acid was also synthesised from malic diamide, by hydrolysis with the calculated quantity of potassium hydroxide or hydrochloric acid. For the acid obtained by both methods, *K* is 0·0286.

K. J. P. O.

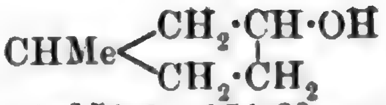
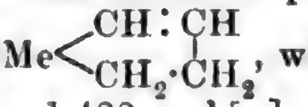
Lead Thiocyanate. By Roy D. Hall (*J. Amer. Chem. Soc.*, 1902, **24**, 570—573).—Pure lead thiocyanate, obtained from lead nitrate and potassium thiocyanate, is not yellow, as stated by Liebig (*Annalen*, 1838, **25**, 546), but forms large, transparent, colourless crystals; the product has a yellow colour, however, if the lead nitrate solution contains a salt of bismuth, iron, or mercury. The solubility of lead thiocyanate in water is 3·3 per cent. at 100°, and 0·69 per cent. at 23°.

Basic lead thiocyanate, OH·Pb·CNS, cannot be prepared by boiling the normal salt with water, but is readily obtained by the addition of potassium thiocyanate to a solution of basic lead acetate. It is sparingly soluble in boiling water and separates on cooling in small, acicular crystals. E. G.

Sulphur and Nitrogen Derivatives of Carbon Disulphide; Mixed Iminodithiocarbonic Esters. By Marcel Delépine (*Bull. Soc. Chim.*, 1902, [iii], **27**, 585—587).—By acting on a dithiocarbamate of a primary amine with an alkyl haloid, a dithiourethane, R·NH·CS·SR′, is formed which can be precipitated with water; this is then dissolved in ether and treated with a slight excess of the second alkyl haloid, when the salt of the mixed base soon begins to crystallise out. *Methyl ethyl methyliminodithiocarbonate*, SMe·C(NMe)·SEt, boils at 205—207°; the corresponding *hydriodide* forms colourless crystals very soluble in water, soluble also in absolute alcohol, melting at 75—77°. The *picrate* forms elongated prisms which melt at 103°; the *platinichloride* melts at 163° with decomposition; the *mercurichloride*, $C_5H_{11}NS_2,HCl,2HgCl_2$, is crystalline and melts at about 83°; the *mercuri-iodide*, $C_5H_{11}NS_2,HI,HgI_2$, crystallises from alcohol in long, yellow needles which melt at 100°.

Methyl benzyl methyliminodithiocarbonate, SMe·C(NMe)·S·C_7H_7, is a colourless oil which distils at about 300°, at the same time undergoing alteration; the *hydriodide* forms colourless crystals melting at 106°; the *picrate* is also crystalline and melts at 110—112°; the *mercurichloride* and *mercuri-iodide* are oily; the *platinichloride* is a yellowish-orange coloured crystalline powder which melts at 140°. A. F.

Synthetical Preparation of Carbon Rings. By William H. Perkin, jun. (*Ber.*, 1902, **35**, 2091—2129).—This lecture contains a review and bibliography of the syntheses of mono- and di-cyclic hydrocarbons and their derivatives. G. T. M.

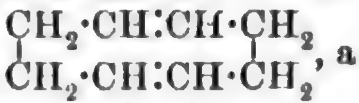
Optically Active Hydrocarbons of the *cyclo*Pentene and *cyclo*Hexene Series. By Nicolai D. Zelinsky (*Ber.*, 1902, **35**, 2488—2494).—1-Methyl-3-*cyclo*pentanone, which has been described by Semmler (Abstr., 1893, i, 129), has the rotation $[\alpha]_D$ +135·9°, although it is derived from β-methyladipic acid, which is only very slightly active. The corresponding *alcohol*,  $CHMe<\begin{matrix}CH_2\cdot CH\cdot OH\\ CH_2\cdot CH_2\end{matrix}$, obtained by the reduction of the ketone, boils at 151·6—151·8°, and has a sp. gr. 0·9122 at 20°/4°, $n_{21^\circ} = 1·4467$, and $[\alpha]_D$ − 4·89°. The alcohol is converted by hydriodic acid into an *iodide*, which boils at 78—80° under 32 mm. pressure and is also slightly lævorotatory. When the iodide is heated with alcoholic potash at 110°, it yields 1-*methyl*-Δ^2-cyclo*pentene*,  $CHMe<\begin{matrix}CH:CH\\ CH_2\cdot CH_2\end{matrix}$, which boils at 69°, has a sp. gr. 0·7663 at 18°/4°, $n_{18^\circ} = 1·422$, and $[\alpha]_D$ + 59·07°. The character of the asymmetric carbon atom of the original ketone is thus preserved throughout the series of changes. The second asymmetric atom present in the alcohol and iodide is of the opposite optical type.

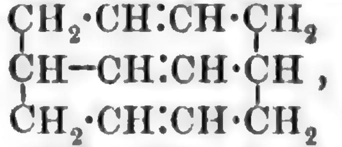
The methyl*cyclo*pentene, obtained by the action of crystallised oxalic acid on 1-methyl-3-*cyclo*pentanol, appears to be a mixture of the foregoing compound with the inactive 1-methyl-3-*cyclo*pentene.

Methyl*cyclo*hexanol is converted by hydriodic acid into 3-*iodo*-1-*methyl*cyclo*hexane*, which boils at 83° under 14 mm. pressure and is optically active. This compound may be made to yield *methyl*cyclo*hexene* in a variety of ways, and the products differ in optical properties. The hydrocarbon obtained by the action of alcoholic potash boils at 103—103·5° (corr.), and has a sp. gr. 0·7937 at 27°/4°, n_{27° 1·4387, and $[\alpha]_D$ 81·47°. This substance seems to be a pure compound, since its properties are not altered by fractional oxidation. The hydrocarbon obtained from the iodide by heating with dimethylaniline boils at 105·5—106·5° (corr.), and has $[\alpha]_D$ 48·29°. A less active substance, with $[\alpha]_D$ 30·3°, is formed by the action of aqueous potassium carbonate on the iodide, and a still less active form, with $[\alpha]_D$ 17·78°, by the action of oxalic acid on the original alcohol.

It seems possible that the high optical activity of these unsaturated ring compounds may be connected with the stereochemical tension which may be supposed to exist in such molecules. A. H.

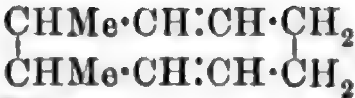
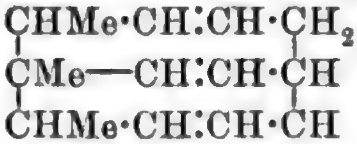
Unsaturated Acids of the Sorbic Acid Series and their Transformation into Cyclic Hydrocarbons. By Oscar Doebner (*Ber.*, 1902, **35**, 2129—2138. Compare this vol., i, 340).

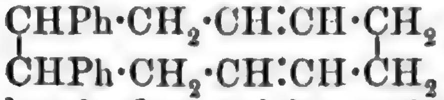
—The distillation of an intimate mixture of β-vinylacrylic acid and anhydrous barium hydroxide gives rise to a mixture of two unsaturated hydrocarbons, cyclo*octa*-$\Delta^{1:5}$-*diene*,  $\begin{matrix}CH_2\cdot CH:CH\cdot CH_2\\ CH_2\cdot CH:CH\cdot CH_2\end{matrix}$, a colourless oil boiling at 50—52° under 17 mm. pressure, having an aromatic odour, a sp. gr. 0·8564, and n_D 1·49646 at 20·7°, and dicyclo*dodecatriene*,



$$\begin{matrix}CH_2\cdot CH:CH\cdot CH_2\\ CH-CH:CH\cdot CH\\ CH_2\cdot CH:CH\cdot CH_2\end{matrix},$$

a yellow oil boiling at 92—95° under 17 mm. pressure, and having a sp. gr. 0·9764 and n_D 1·5378 at 20·7°. The formulæ of these substances are confirmed by the cryoscopic determination of the molecular weights in benzene solution.

Sorbic acid, on distillation with barium hydroxide, also yields a mixture of 3 : 4-*dimethyl*cyclo*octa*-$\Delta^{1:5}$-*diene*,  $\begin{array}{l}\text{CHMe}\cdot\text{CH:CH}\cdot\text{CH}_2\\ |\qquad\qquad\qquad\quad|\\ \text{CHMe}\cdot\text{CH:CH}\cdot\text{CH}_2\end{array}$, and *trimethyl*dicyclo*dodecatriene*,  $\begin{array}{l}\text{CHMe}\cdot\text{CH:CH}\cdot\text{CH}_2\\ |\qquad\qquad\qquad\quad|\\ \text{CMe}\text{---}\text{CH:CH}\cdot\text{CH}\\ |\qquad\qquad\qquad\quad|\\ \text{CHMe}\cdot\text{CH:CH}\cdot\text{CH}\end{array}$; the former is a colourless oil boiling at 68—71° under 15 mm. pressure, having a sp. gr. 0·8623 and n_D 1·49036 at 13°; it has a faintly aromatic odour and its molecular weight corresponds with the formula $C_{10}H_{16}$. The latter hydrocarbon is a yellowish-green, highly refractive oil boiling at 85—87° under 15 mm. pressure; it has a sp. gr. 0·9442 and n_D 1·53321 at 15·5°.

Cinnamenylacrylic acid, CHPh:CH·CH:CH·CO_2H, prepared by heating together cinnamaldehyde, malonic acid, and pyridine, when distilled with barium hydroxide, yields an oily mixture of *a-phenylbuta*-$\Delta_{a:\gamma}$-*diene*, CHPh:CH·CH:CH_2, and 3 : 4-*diphenyl*cyclo*octa*-$\Delta^{1:5}$-*diene*,  $\begin{array}{l}\text{CHPh}\cdot\text{CH}_2\cdot\text{CH:CH}\cdot\text{CH}_2\\ |\qquad\qquad\qquad\qquad\quad|\\ \text{CHPh}\cdot\text{CH}_2\cdot\text{CH:CH}\cdot\text{CH}_2\end{array}$; the former crystallises from ether in colourless leaflets melting at 25° and boiling at 120—122° under 10 mm. pressure; the latter is a yellowish-green, oily liquid with a blue fluorescence boiling at 204—205° under 10 mm. pressure; it has a sp. gr. 1·018 at 15·3°.

3 : 4-*Diphenyl*cyclo*octa*-$\Delta^{1:5}$-*diene* does not combine with bromine and is very slowly attacked by acid or alkaline solutions of permanganate; after 8 days' digestion with the hot oxidising agent, it yields only a trace of benzoic acid.

G. T. M.

Action of Ammonia on αβ-Dichlorostyrenes. By Franz Kunckell and Franz Vossen (*Ber.*, 1902, **35**, 2294—2295).—2 : 5-Diphenylpyrazine (Staedel and Rügheimer, *Ber.*, 1876, **9**, 563) is readily obtained when αβ-dichlorostyrene is heated with excess of concentrated ammonia in sealed tubes at 180—200° for 12—18 hours. 2 : 5-*Di* p-*tolylpyrazine*, obtained by the action of ammonia on αβ-dichloro-*p*-methylstyrene, crystallises in colourless plates melting at 204°.

J. J. S.

Salts of *m*-Benzenedithiosulphonic Acid. By Julius Troeger and W. Meine (*Ber.*, 1902, **35**, 2164—2168).—By gradually adding *m*-benzenedisulphonic chloride to a concentrated aqueous solution of potassium disulphide, a solution is obtained which, after filtering and cooling, deposits crystals mainly consisting of *potassium* m-*benzenedithiosulphonate*; the pure salt can be obtained as a syrup, which gradually solidifies to a hygroscopic mass, by extracting the crude substance with alcohol and evaporating the solution. The *silver* salt, $C_6H_4(SO_2\cdot SAg)_2$, is a white powder which is insoluble in ammonia. The *sodium* salt resembles the potassium salt; the *berberine* salt,

$$C_6H_4(SO_2\cdot SH,C_{20}H_{17}O_4N)_2,$$

is a yellow precipitate; the *strychnine* salt, $C_6H_4(SO_2\cdot SH,C_{21}H_{22}O_2N_2)_2$, separates from water in white crystals and melts and decomposes at 252°.

On decomposing a solution of potassium *m*-benzenedithiosulphonate with concentrated hydrochloric acid, sulphur is precipitated, and on evaporating the filtrate a white, insoluble *substance*, $C_6H_4S_2O_2$, separates; this is apparently formed by the decomposition of the disulphinic acid initially produced.

With alcoholic sodium β-thionaphthoxide, *m*-benzenedisulphonic chloride gives β-naphthyl disulphide. W. A. D.

Triphenylmethyl. V. Carbonium Salts.

By MOSES GOMBERG (*Ber.*, 1902, **35**, 2397—2408).—Determinations of the freezing point of solutions of triphenylchloromethane in benzene gave no evidence of dissociation, whilst boiling point measurements indicated association. When dissolved in liquid sulphur dioxide, however, this series of compounds exhibits an appreciable conductivity which is very marked in the case of triphenylbromomethane. The formation of perhaloids and double salts is also regarded as evidence for the salt-like character of these compounds, whilst the basic character of triphenylcarbinol is deduced from the readiness with which it forms the chloride when treated with hydrogen chloride.

Triphenylmethyl is colourless when solid, but is yellow in solution like the salts of triphenylcarbinol. A theory of 'pseudo-dissociation' with formation of 'pseudo-ions' is advanced to account for this.

T. M. L.

Bromination and Nitration in the Aromatic Series.

By JAN JOHANNES BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 643—647. Compare this vol., i, 442).—*p*-Nitromethylaniline gives trinitrophenol when treated with nitric acid of sp. gr. 1·52. On treatment with 1 mol. of bromine, it gives 2-*bromo*-4-*nitromethylaniline*, which melts at 118°, whilst with 2 mols. of bromine it yields 2 : 6-*dibromo*-4-*nitromethylaniline* melting at 113°. The former of these bromine compounds, when treated with nitric acid, gives 2-*bromo*-4 : 6-*dinitrophenylmethylnitroamine* (m. p. 125°), and the latter 2 : 6-*dibromo*-4-*nitrophenylmethylnitroamine* (m. p. 84°).

o-Nitromethylaniline likewise gives a trinitrophenylmethylnitroamine when treated with nitric acid, which is converted into 4-*bromo*-2-*nitromethylaniline* (m. p. 101°), then into 4 : 6-*dibromo*-2-*nitromethylaniline* (m. p. 100°) by the action of bromine. With nitric acid, the former bromine compound gives 4-*bromo* 2 : 6-*dinitrophenylmethylnitroamine* (m. p. 109°), the latter 2 : 4-*dibromo*-6-*nitrophenylmethylnitroamine* (m. p. 90°).

2 : 4-Dinitro-6-cyano-1-ethoxybenzene, when treated in alcoholic solution with methylamine or ethylamine, has the ethoxy-group replaced by the methylamino- or ethylamino-group, and by the action of nitric acid on the resulting product the corresponding nitroamine is formed.

The author concludes that: (1) on brominating alkylanilines, bromine enters into the free ortho- and para-positions, whilst the hydrogen atom attached to the nitrogen is not attacked. The same applies to the action of nitric acid, but the amino-hydrogen is simultaneously replaced by the nitro-group. (2) A carboxyl group in the ortho- or para-position is replaced by Br or NO_2 with evolution of carbon dioxide, and (3) the occupation of the meta-position has no influence on the introduction of Br or NO_2 into the ortho- and para-positions.

The author explains these results as the effect of indirect substitutions. In the bromination or nitration of phenol or aniline, the halogen or NO_2 group first enters the side chain, then shifts to the nucleus. In indirect substitution, the substituting groups always enter the ortho- or para-positions, whilst by direct substitution meta-compounds may be produced. During direct substitution, some groups (CO_2H, Me, $CH_2{\cdot}OH$, SO_3H) may be expelled from the ortho- or para-position. J. McC.

Some Salts of Benzylamine. By René Dhommée (*Compt. rend.*, 1902, **134**, 1313—1314).—*Benzylamine nitrate*, $CH_2Ph{\cdot}NH_2,HNO_3$, is obtained from benzylamine and dilute nitric acid in the form of colourless, hexagonal plates which melt at 136°. One hundred c.c. of water at 19° dissolve 28·6 grams, 100 c.c. of alcohol 20·7 grams.

Benzylamine sulphate, $CH_2Ph{\cdot}NH_2,H_2SO_4$, crystallises in colourless needles which melt at 93°. One hundred c.c. of water at 19° dissolve 60·6 grams, 100 c.c. of acetone 32·4 grams, and 100 c.c. of 95 per cent. alcohol 26·0 grams. It is insoluble in ether.

Benzylamine borate, $CH_2Ph{\cdot}NH_2,2B_2O_3,1\frac{1}{2}H_2O$, forms colourless plates which decompose without fusing at about 200°. At 19°, 100 c.c. of water dissolve 12·2 grams, 100 c.c. of alcohol 1·9 grams, and 100 c.c. of acetone 0·54 gram. It is quite insoluble in ether.

Benzylamine chromate, $(CH_2Ph{\cdot}NH_2)_2CrO_3,2H_2O$, is obtained in golden-yellow plates which do not melt but decompose at 60°. It is insoluble in alcohol and is decomposed by acetone or ether. One hundred c.c. of water at 19° dissolve 4·99 grams.

Benzylamine oxalate, $(CH_2Ph{\cdot}NH_2)_2,H_2C_2O_4$, forms colourless prisms which melt at 195°. At 15°, 100 c.c. of water dissolve 7·39 grams, 100 c.c of 95 per cent. alcohol 0·05 gram, and it is insoluble in acetone or ether.

Benzylamine benzoate, $CH_2Ph{\cdot}NH_2,C_7H_6O_2$, crystallises from alcohol in colourless prisms melting at 132—134°. At 19°, 100 c.c. of 95 per cent. alcohol dissolve 8·76 grams, 100 c.c. of ether 0·2 gram, and 100 c.c. of water 0·03 gram. It is decomposed by acetone. J. McC.

Action of Nitric Acid on Alkylated Amines of *p*-Toluenesulphonic Acid. By Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 616—618. Compare *Rec. Trav. Chim.*, 1884, **3**, 7).—*p*-Toluenesulphonmethylamide melts at 76—77°, the monoethyl compound at 64°, the *dimethyl* derivative at 76°, and the *diethyl* derivative at 59—60°.

The monomethyl compound, when dissolved in nitric acid of sp. gr. 1·48, gives *nitro*-p-*toluenesulphonmethylnitroamide* (m. p. 116°) and p-*toluenesulphonmethylnitroamide* (m. p. 60°). With acid of sp. gr. 1·52 only the former is produced. With nitric acid of sp. gr. 1·52, the monoethyl derivative gives *nitro*-p-*toluenesulphonethylnitroamide* (m. p. 76°); this is decomposed by sulphuric acid, nitrous oxide being evolved and a nitro-*p*-toluenesulphonic acid produced the barium salt of which crystallises with 2 mols. of water.

With nitric acid of sp. gr. 1·48, *p*-toluenesulphondimethylamide yields dimethylamide (? dinitro-dimethylamide) melting at 57°, whilst the diethyl compound with nitric acid of sp. gr. greater than 1·5 gives *nitro*-p-*toluenesulphonethylnitroamide* (m. p. 76°).

By the action of chlorosulphonic acid on nitrotoluene, a nitrotoluenesulphonic chloride is obtained which with ammonia gives an amine melting at 140°. With potassium nitrotoluenesulphonate, obtained by the action of fuming sulphuric acid on nitrotoluene, phosphorus pentachloride gives a sulphonic chloride from which two amines are produced with ammonia; one of these melts at 141°. *p*-Toluenesulphonic chloride and fuming nitric acid yield a nitro-derivative which can be recrystallised from light petroleum and melts at 45°; the nitro-group enters the ortho-position with reference to the methyl group. It gives an amide melting at 143°. By acting on the 2-nitrotoluene-4-sulphonic chloride with methylamine or ethylamine followed by treatment with nitric acid, the nitro-*p*-toluenesulphonmethylnitroamide previously mentioned (or the ethyl derivative) have been obtained, proving that in these the grouping is

$$[\mathrm{Me\ (or\ Et)} : \mathrm{NO_2} = 1 : 2.]$$

J. McC.

Preparation and Reactions of Derivatives of Formamidines.

By Frank B. Dains (*Ber.*, 1902, **35**, 2496—2511).—The compound $NH\colon CH{\cdot}NH{\cdot}CHCl_2,HCl$, obtained by the interaction of hydrogen chloride and cyanide in benzene solution (see Gattermann and Schnitzspahn, Abstr., 1898, i, 546), reacts with 2 mols. of a primary amine, forming formamidine and a disubstituted formamidine, $NR\colon CH{\cdot}NHR$.

Aniline, *m*- and *p*-nitroanilines, the toluidines, *a*-naphthylamine, anisidine, phenetidine, and aminoazobenzene all react with this compound yielding formamidines which have been previously obtained from ethyl orthoformate; *o*-nitroaniline, *p*-aminophenol, and benzidine do not react.

Di-p-*chlorophenylformamidine* crystallises from benzene in white needles, melts at 179°, and forms a *picrate* which crystallises in slender, yellow needles and melts and decomposes at 242°.

Di-m-*xylylformamidine* crystallises in white needles and melts at 131°; its *hydrochloride*, *platinichloride*, and *picrate* melt and decompose at 243°, 201°, and 228° respectively. *Di-ψ-cumylformamidine* crystallises in slender, white needles, melts at 160°, and forms a *hydrochloride* melting at 236°. *Di-β-naphthylformamidine* crystallises in slender, white needles and melts at 186°.

Phenylhydrazine and *o*-phenylenediamine react with the compound, forming phenylazophenylhydrazonemethane and benziminoazole respectively.

The disubstituted formamidines react with compounds containing a methylene group, forming compounds of the type $R{\cdot}NH{\cdot}CH\colon CXY$, which have been previously obtained by treating the compounds $CXY\colon CH{\cdot}OEt$ with primary amines. When Y represents a carbethoxy-group, compounds of the type $R{\cdot}NH{\cdot}CH\colon CX{\cdot}CO{\cdot}NHR$ are obtained.

The following new compounds are described. m-*Xylidinomethylene*-

acetylacetone, $C_6H_3Me_2\cdot NH\cdot CH\colon C(COMe)_2$, crystallises in hairy needles melting at 146°. p-*Toluidinomethylenebenzyl cyanide* crystallises in bright brown needles melting at 135°, and the corresponding m-*xylidino*-compound melts at 130°. The o-*toluidide* of ethyl *o*-toluidinomethylene-malonate, $C_6H_4Me\cdot NH\cdot CH\colon C(CO_2Et)\cdot CO\cdot NH\cdot C_6H_4Me$, melts at 161°, and the corresponding *acid* melts and decomposes at 161°, yielding the o-*toluidide* of *o*-toluidinoacrylic acid. The analogous *compound* from di-*p*-tolylformamidine melts at 168° and when hydrolysed yields an *acid* melting at 187°; the analogous *compounds* from di-*m*-xylyl-, di-ψ-cumyl-, di-*p*-chlorophenyl-, di-*p*-anisyl-formamidines melt respectively at 147° (slender, white needles), at 180°, at 176°, and at 130°. The o-*tolyl* compound, $C_6H_4Me\cdot NH\cdot CH\colon C(COMe)\cdot CO\cdot NH\cdot C_6H_4Me$ (from di-*o*-tolylformamidine and ethyl acetoacetate), crystallises in needles and melts at 172°, and the analogous *p*-tolyl and *p*-xylyl compounds melt respectively at 170° and 188°. The p-*tolyl* compound,

$$C_6H_4Me\cdot NH\cdot CH\colon C(CN)\cdot CO_2Et$$

(from di-*p*-tolylformamidine and ethyl cyanoacetate), melts at 137°, and the analogous o-*tolyl* and ψ-*cumyl* derivatives at 137—138° and 195° respectively. R. H. P.

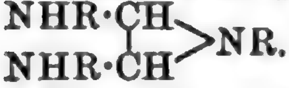
Action of Phenylcarbimide on the Esters of some Oxy-acids. II.

By Eugène Lambling (*Bull. Soc. Chim.*, 1902, [iii], **27**, 606—611. Compare this vol., i, 537).—On heating together at 135—140° ethyl a-hydroxybutyrate and phenylcarbimide, a reddish-brown oil is obtained, which, however, cannot be distilled without decomposition, and does not crystallise. Its reactions show it to be the *phenylurethane* of *ethyl a-hydroxybutyrate*, $CH_2Me\cdot C(OH)(CO_2H)\cdot CO\cdot NHPh$. When saponified with an aqueous solution of sodium hydroxide, the *phenylurethane* of *a-hydroxybutyric acid* is obtained which forms microscopic prisms melting and decomposing at 116·5—117·5°; it is very soluble in alcohol or ether and soluble in hot benzene or chloroform. The *lactam*, obtained by heating this acid, forms very slender, microscopic needles which melt at 88°; it is very sparingly soluble in cold water, more soluble in boiling water with partial retransformation into the acid, soluble also in alcohol, ether, benzene, or chloroform.

In a similar manner, the *phenylurethane* of *ethyl a-hydroxyvalerate* has been obtained only in the form of an oil. On boiling this oil with a solution of sodium hydroxide, the alkaline solution deposits on cooling crystals of diphenylcarbamide and of normal *a-hydroxyvaleranilide*. The latter substance, which has also been synthesised by heating aniline with valeric acid, forms pearly scales soluble in boiling water, alcohol, ether, chloroform, or benzene, and melting at 89—90°. On acidifying the alkaline solution, the *phenylurethane* of *a-hydroxyvaleric acid* is obtained in the form of white, prismatic crystals melting at 78°; it is sparingly soluble in cold water, more soluble in boiling water with partial transformation into its lactam, very soluble in alcohol, ether, chloroform, or benzene, much less so in light petroleum. When boiled with water, the *lactam* is formed together with the anilide; the lactam forms elongated, slender prisms which melt at 95—96° and are soluble in alcohol, ether, chloroform, or benzene, sparingly so in light petroleum.

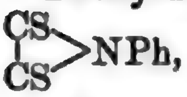
The *phenylurethane* of *ethyl a-hydroxyisovalerate*, obtained in a manner similar to the preceding compounds, forms a mass of crystalline needles which, however, have not been obtained quite pure. On boiling with a solution of sodium hydroxide, there are formed the *anilide* of a-hydroxy*iso*valeric acid which crystallises in characteristic microscopic octahedra melting at 133°, and the *phenylurethane* of *a-hydroxyisovaleric acid* which crystallises in microscopic, slender needles melting at 111—112°; it is soluble in alcohol, ether, chloroform, or benzene, sparingly so in light petroleum. The corresponding *lactam* forms slender needles which melt at 66—67° and are soluble in alcohol, ether, or benzene. A. F.

Cyclic *iso*Nitriles and their Derivatives. II, III, and IV. By ALEXANDER P. SABANÉEF, E. RAKOWSKY and M. PROSIN (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 398—404, 404—408, 408—410. Compare Abstr., 1901, i, 695).—The authors have investigated the best conditions for preparing acetylenetriphenyltriamine by the action of aniline and potassium hydroxide on acetylene dibromide or tetrabromide or on tribromoethylene. The phenyldicarbylamine also formed in the reaction combines with primary amines, yielding cyclic amidines of the type

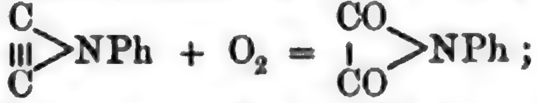


$\begin{matrix}NHR\cdot CH\\ |\\ NHR\cdot CH\end{matrix}>NR.$

Phenyldicarbylamine combines with sulphur, forming dithio-oxanil,

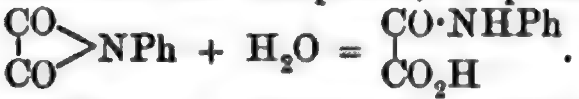


$\begin{matrix}CS\\ |\\ CS\end{matrix}>NPh$, which is capable of uniting with a molecule of aniline, yielding dithio-oxanilide, NHPh·CS·CS·NHPh, formerly obtained by Wallach (Abstr., 1880, 556). Phenyldicarbylamine is also readily oxidised according to the equation:



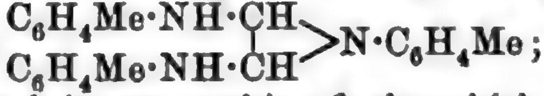
$\begin{matrix}C\\ |||\\ C\end{matrix}>NPh + O_2 = \begin{matrix}CO\\ |\\ CO\end{matrix}>NPh$;

and the last compound, in presence of water, yields oxanilic acid:



$\begin{matrix}CO\\ |\\ CO\end{matrix}>NPh + H_2O = \begin{matrix}CO\cdot NHPh\\ |\\ CO_2H\end{matrix}$.

When a mixture of *p*-toluidine with acetylene tetrabromide is treated with alcoholic potassium hydroxide, *p*-tolyldicarbylamine is first formed, and this combines with *p*-toluidine, yielding a cyclic *amidine* of the constitution



$\begin{matrix}C_6H_4Me\cdot NH\cdot CH\\ |\\ C_6H_4Me\cdot NH\cdot CH\end{matrix}>N\cdot C_6H_4Me$;

this compound separates from alcohol in snow-white flocks which darken at 132° and melt at about 145°. It dissolves readily in acids, forming salts: the *hydrochloride*, $C_{23}H_{25}N_3,2HCl$, and the *platinichloride*, $C_{23}H_{25}N_3,H_2PtCl_6$, were prepared and analysed. *p*-Tolyldicarbylamine also unites with sulphur, yielding *dithio-oxal-*p*-toluidide*,

$$C_2S_2(NH\cdot C_6H_4Me)_2,$$

which crystallises from alcohol in golden-yellow, shining plates melting at 150°. T. H. P.

Iminoxanthides, a New Class of Coloured Organic Compounds. By L. TSCHUGAEFF (*Ber.*, 1902, **35**, 2470—2473).—Aromatic iminochlorides of the type R′·CCl:NR″ react with the sodium salts of the xanthic esters, $\mathrm{R'''O\cdot CS\cdot SNa}$, to form iminoxanthides, $\mathrm{NR'':CR'\cdot S\cdot CS\cdot OR'''}$. These compounds are coloured various shades of red, but are not dyes, the chromophoric group being probably $[\mathrm{\cdot CS\cdot S\cdot C:N}]$. They are neutral substances without any basic properties, and by hydrolysis are resolved into the corresponding alcohol, acid and base. The following have been prepared :—1 : 2-*Diphenyl*-3-*ethyliminoxanthide*, $\mathrm{NPh\cdot CPh\cdot S\cdot CS\cdot OEt}$, forms garnet-red prisms melting 98—98·5°, and yields aniline, benzoic acid, and ethyl alcohol on hydrolysis. 1 : 2-*Diphenyl*-3-l-*menthyliminoxanthide*,

$$\mathrm{NPh:CPh\cdot S\cdot CS\cdot O\cdot C_{10}H_{19}},$$

forms orange-red, matted needles melting at 105—106°. 1 : 2-*Diphenyl*-3-*bornyliminoxanthide*, $\mathrm{NPh:CPh\cdot S\cdot CS\cdot O\cdot C_{10}H_{17}}$, was prepared in both its optically isomeric forms; these are identical in appearance and melting point, and crystallise extremely well in bright red prisms melting at 87—88°. The inactive racemic form separates in small, red crystals and melts at 89—90°. 1 : 2-*Diphenyl*-3-*fenchyliminoxanthide*, forms small, brownish-red crystals melting at 84—85°. This compound is isomeric with bornyliminoxanthide, but differs from it remarkably in colour. 1 : 2-*Diphenyl*-3-*benzyliminoxanthide*, $\mathrm{NPh:CPh\cdot S\cdot CS\cdot O\cdot C_7H_7}$, forms long, matted, ponceau-red needles melting at 72—73°. 1-*Phenyl*-2-o-*tolyl*-3-*ethyliminoxanthide*,

$$\mathrm{C_6H_4Me\cdot N:CPh\cdot S\cdot CS\cdot OEt},$$

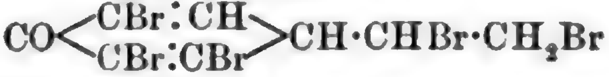
crystallises in scarlet prisms melting at 76—77°. 1-*Phenyl*-2-ψ-*cumyliminoxanthide*, $\mathrm{C_6H_2Me_3\cdot N:CPh\cdot S\cdot CS\cdot OEt}$, forms dark red tablets melting at 96—97°.

The iminoxanthides of the terpene series are the first examples, other than salts, of optically active substances which are strongly coloured. A. H.

The Phenols from Shale Oil. By THOMAS GRAY (*J. Soc. Chem. Ind.*, 1902, 21, 845—847).—" Green naphtha " creosote from shale oil contains 5—6 per cent. of phenol, and 12—15 per cent. of *o*-cresol, but the bulk of the mixture is composed of *m*-cresol and xylenols, which seem to be present in approximately equal quantity, namely, 30—35 per cent.; of the xylenols, the isomerides having the configuration $[\mathrm{Me_2:OH = 1:2:4}$ and $= 1:3:5]$ have been identified. Sixteen per cent. of the total phenols are present in the fraction boiling above 230°. Cresol and *p*-cresol seem to be absent, and guaiacol is present in very small quantity. L. DE K.

Action of Bromine and Chlorine on Phenols, Substitution Products, ψ-Bromides, and ψ-Chlorides. By THEODOR ZINCKE, O. SIEBERT, and H. REINBACH (*Annalen*, 1902, 322, 174—238. Compare this vol., i, 282).—*Tribromo*-p-*ethylphenol*, $\mathrm{C_6HEtBr_3\cdot OH}$, readily obtained by adding bromine to a chloroform solution of *p*-ethylphenol in the presence of iron wire, crystallises in flattened, silky needles melting at 54—55°; it is readily soluble in dilute sodium hydroxide solution and yields an *acetyl* derivative separating in lustrous, monoclinic crystals melting at 70°. Tetrabromo-*p*-ethylphenol, $\mathrm{C_6EtBr_4\cdot OH}$, although obtained by Fittig and Kiesow by adding bromine to powdered *p*-ethylphenol, is prepared with greater certainty by operating in chloroform solution in the presence of iron wire; if aluminium is employed, no solvent is required; it crystallises in white needles and melts at 109—110°; its *acetyl* derivative crystallises from glacial acetic acid and melts at 133—134°.

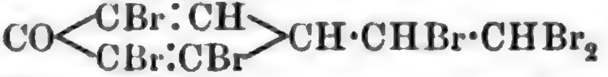
αβ-2 : 3 : 5-Pentabromo-*ψ*-*p*-ethylphenol,



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CBr}\end{matrix}\Big\rangle\mathrm{CH{\cdot}CHBr{\cdot}CH_2Br}$$

or $OH\cdot C_6HBr_3\cdot CHBr\cdot CH_2Br$, is conveniently prepared by heating tribromo-*p*-ethylphenol with the theoretical amount of bromine under pressure at 100°; it crystallises from a mixture of light petroleum and benzene either in spherical aggregates of needles melting at 129°, or in prisms melting at 131°. This substance may also be prepared either by adding bromine to tribromo-*p*-vinylphenol, or hydrogen bromide to tribromo-*β*-bromo-*p*-vinylphenol; it does not behave like a phenol, and dissolves only slowly in solutions of the alkali hydroxides with decomposition.

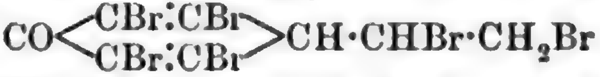
αββ-2 : 3 : 5-*Hexabromo*-*ψ*-p-*ethylphenol*,



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CBr}\end{matrix}\Big\rangle\mathrm{CH{\cdot}CHBr{\cdot}CHBr_2}$$

or $OH\cdot C_6HBr_3\cdot CHBr\cdot CHBr_2$, produced either by heating the pentabromide or the tribromo-compound with bromine at 100°, or by adding the halogen to 2 : 3 : 5-*β*-tetrabromo-*p*-vinylphenol, crystallises in needles melting at 131—132°; it slowly dissolves in solutions of the alkali hydroxides, becoming soluble more rapidly in the presence of acetone; with concentrated sulphuric acid, it develops a deep red coloration.

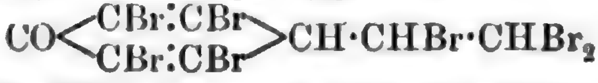
αβ-2 : 3 : 5 : 6-*Hexabromo*-*ψ*-p-*ethylphenol*,



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}\Big\rangle\mathrm{CH{\cdot}CHBr{\cdot}CH_2Br}$$

or $OH\cdot C_6Br_4\cdot CHBr\cdot CH_2Br$, obtained by heating tetrabromo-*p*-ethylphenol with the theoretical amount of bromine at 120—160°, separates from a mixture of benzene and light petroleum in crystals melting at 179°; it dissolves in alkali hydroxide solutions, but only in the presence of acetone.

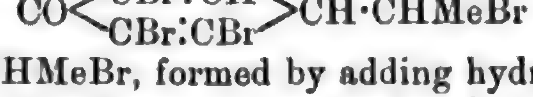
αββ-2 : 3 : 5 : 6-*Heptabromo*-*ψ*-p-*ethylphenol*,



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}\Big\rangle\mathrm{CH{\cdot}CHBr{\cdot}CHBr_2}$$

or $OH\cdot C_6Br_4\cdot CHBr\cdot CHBr_2$, formed from tetrabromo-*p*-ethylphenol by the action of excess of bromine at 130—140°, crystallises in lustrous rhombohedra and melts at 174°. The substance is readily converted into an ethylidenequinone containing six bromine atoms; zinc and hydrogen bromide in ether reduce it to bromo-*p*-vinyltetrabromophenol.

2 : 3 : 5-*Tribromo*-p-*vinylphenol*, $OH\cdot C_6HBr_3\cdot CH{:}CH_2$, obtained by reducing *αβ*-2 : 3 : 5-pentabromo-*ψ*-*p*-ethylphenol with granulated zinc and hydrogen bromide, crystallises from light petroleum or 80 per cent. acetic acid in colourless leaflets or needles melting at 93—94°; the *acetyl* compound separates in nodular aggregates melting at 86—87°. *α*-2 : 3 : 5-*Tetrabromo*-*ψ*-p-*ethylphenol*,



$$\mathrm{CO}\Big\langle\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CBr}\end{matrix}\Big\rangle\mathrm{CH{\cdot}CHMeBr}$$

or $OH\cdot C_6HBr_3\cdot CHMeBr$, formed by adding hydrogen bromide to the vinyl compound, crystallises in plates and melts at 87°. The addition of bromine leads to the regeneration of the pentabromo-*ψ*-phenol.

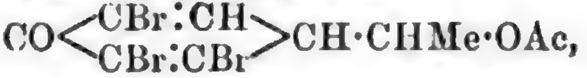
β-2 : 3 : 5-*Tetrabromo*-p-*vinylphenol*, $OH\cdot C_6HBr_3\cdot CH{:}CHBr$, prepared from the hexabromide, crystallises from a mixture of benzene and petroleum in colourless needles and melts at 167° ; the *acetyl* compound forms white leaflets and melts at 155° ; it yields the original hexabromide on adding bromine, and the addition of hydrogen bromide leads to the production of the pentabromo-compound melting at 129—131°.

β-2 : 3 : 5 :6-*Pentabromo*-p-*vinylphenol*, $OH\cdot C_6Br_4\cdot CH{:}CHBr$, prepared from the heptabromo-compound, crystallises in needles and melts at 170—171° ; its *sodium* salt is sparingly soluble, and its *acetyl* compound melts at 172° ; the heptabromide is regenerated by the addition of bromine.

2 : 3 : 5-*Tribromo-α-hydroxy*-p-*ethylphenol*, $OH\cdot C_6HBr_3\cdot CHMe\cdot OH$, obtained by heating the corresponding tetrabromo-derivative with dilute acetone, crystallises in needles melting at 117—118° ; it dissolves in the alkali hydroxides without decomposition and is soluble in the ordinary organic solvents ; its *diacetyl* derivative crystallises from glacial acetic acid in colourless needles and melts at 71°.

2 : 3 : 5-*Tribromo-α-methoxy*-p-*ethylphenol*, $OH\cdot C_6HBr_3\cdot CHMe\cdot OMe$, produced by heating the tetrabromo-compound with methyl alcohol separates from light petroleum in spherical aggregates melting at 97°.

2 : 3 : 5-*Tribromo-α-acetoxy*-p-*ethylphenol*,



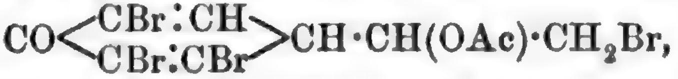
$$CO<\begin{matrix}CBr{:}CH\\ CBr{:}CBr\end{matrix}>CH\cdot CHMe\cdot OAc,$$

prepared by heating the tetrabromide with glacial acetic acid and sodium acetate, forms white crystals melting at 186—187° ; it dissolves in the ordinary organic solvents, but is decomposed by alkali hydroxide solutions.

β-2 : 3 : 5-*Tetrabromo-α-hydroxy*-p-*ethylphenol*,

$$OH\cdot C_6HBr_3\cdot CH(OH)\cdot CH_2Br,$$

obtained from the pentabromide by the action of dilute acetone, crystallises in plates and melts at 147—148° ; it is decomposed by alkali hydroxides ; the *acetyl* derivative,



$$CO<\begin{matrix}CBr{:}CH\\ CBr{:}CBr\end{matrix}>CH\cdot CH(OAc)\cdot CH_2Br,$$

or $OH\cdot C_6HBrCH(OAc)CH_2Br$, prepared by boiling the pentabromide with glacial acetic acid and sodium acetate ; it melts at 164—165° and yields the *diacetyl* compound on treatment with acetic anhydride ; this substance separates from light petroleum in acicular crystals melting at 110—111°.

β-2 : 3 : 5-*Tetrabromo-α-methoxy*-p-*ethylphenol*,

$$OH\cdot C_6HBr_3\cdot CH(OMe)\cdot CH_2Br,$$

resulting from the interaction of methyl alcohol and the pentabromide, crystallises in thick needles and melts at 133—134° ; its *acetyl* derivative crystallises in yellow needles and melts at 90—91°.

αβ-2 : 3 : 5-*Pentabromo*-p-*ethylphenyl acetate*,

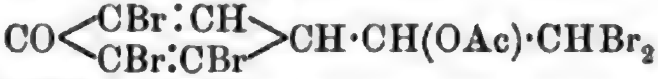
$$OAc\cdot C_6HBr_3\cdot CHBr\cdot CH_2Br,$$

prepared by heating the pentabromide with acetic anhydride, separates in monoclinic crystals and melts at 143—144°.

ββ-2 : 3 : 5-*Pentabromo-α-hydroxy*-p-*ethylphenol*,

$$OH\cdot C_6HBr_3\cdot CH(OH)\cdot CHBr_2,$$

obtained from the hexabromide, forms lustrous, monoclinic crystals melting at 125—126 ; its *acetyl* derivative,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CBr}\end{matrix}{>}\mathrm{CH{\cdot}CH(OAc){\cdot}CHBr_2}$$

or $OH{\cdot}C_6HBr_3{\cdot}CH(OAc){\cdot}CHBr_2$, also separates in monoclinic crystals melting at 128—129 ; its *diacetyl* compound crystallises in needles and melts at 131—132°.

ββ-2 : 3 : 5-*Pentabromo-α-methoxy*-p-*ethylphenol*,

$$OH{\cdot}C_6HBr_3{\cdot}CH(OMe){\cdot}CHBr_2,$$

separates in white, spherical aggregates and its acetyl derivative in white needles, they melt at 120° and 150—151° respectively.

αββ-2 : 3 : 5-*Hexabromo*-p-*ethylphenyl acetate*,

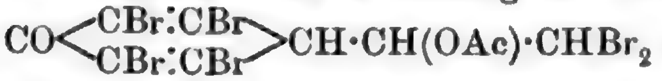
$$OAc{\cdot}CHBr_3{\cdot}CHBr{\cdot}CHBr_2,$$

prepared by heating the hexabromide with acetic anhydride, crystallises in plates and melts at 116—117°.

ββ-2 : 3 : 5 : 6-*Hexabromo-α-hydroxy*-p-*ethylphenol*,

$$OH{\cdot}C_6Br_4{\cdot}CH(OH){\cdot}CHBr_2,$$

obtained by warming the heptabromide with dilute acetone, crystallises in colourless needles melting at 156—157° ; the *acetyl* derivative,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}{>}\mathrm{CH{\cdot}CH(OAc){\cdot}CHBr_2}$$

or $OH{\cdot}C_6Br_4{\cdot}CH(OAc){\cdot}CHBr_2$, is produced by heating the heptabromide with acetic anhydride, the *diacetyl* compound is the result of more prolonged action in the presence of sodium acetate ; they separate in colourless crystals melting respectively at 177—178° and 124—125°.

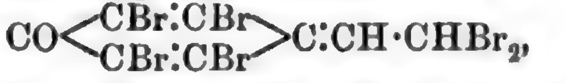
ββ-2 : 3 : 5 : 6-*Hexabromo-α-methoxy*-p-*ethylphenol*,

$$OH{\cdot}C_6Br_4{\cdot}CH(OMe){\cdot}CHBr_2,$$

obtained by boiling the heptabromide with methyl alcohol, separates in rhombohedral crystals and melts at 109—110°.

αββ-2 : 3 : 5 : 6-*Heptabromo*-p-*ethylphenol*, $OAc{\cdot}C_6Br_4{\cdot}CHBr{\cdot}CHBr_2$, prepared by warming the heptabromide with acetic anhydride for a short time, separates from glacial acetic acid in lustrous crystals melting at 129—130°.

ββ-2 : 3 : 5 : 6-*Hexabromo*-p-*ethylidenequinone*,



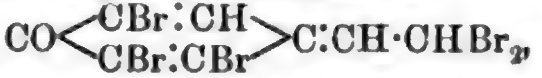
$$\mathrm{CO}{<}\begin{matrix}\mathrm{CBr{:}CBr}\\ \mathrm{CBr{:}CBr}\end{matrix}{>}\mathrm{C{:}CH{\cdot}CHBr_2},$$

produced by shaking a 10 per cent. sodium acetate solution with the heptabromide dissolved in petroleum and dry ether, is a deep yellow, crystalline powder sintering at 180° and melting at 230—235° ; when treated with solvents, it readily decomposes, yielding a white, amorphous substance. It readily forms additive products, thus on treatment with water, methyl alcohol, or acetic anhydride it yields ββ-2 : 3 : 5 : 6-hexabromo-α-hydroxy-*p*-ethylphenol, ββ-2 : 3 : 5 : 6-hexabromo-α-methoxy-*p*-ethylphenol, and ββ-2 : 3 : 5 : 6-hexabromo-α-acetoxy-*p*-ethylphenyl acetate respectively. The heptabromide is regenerated by the addition of hydrogen bromide, and β-2 : 3:5:6-pentabromo-*p*-vinylphenol results from the action of zinc and an ethereal hydrogen bromide solution.

The white, amorphous *compound*, $C_8H_2Br_6O$, sinters at 150—155° and melts at 165° ; it is far less reactive than the quinone, but nevertheless slowly forms additive products with acetic anhydride and water which are identical with those obtained from the quinone.

The heptabromide yields a white, insoluble product when its ethereal solution is shaken with anhydrous sodium acetate; this *compound*, $C_8H_2Br_6O$, is an amorphous powder decomposing at about 200°.

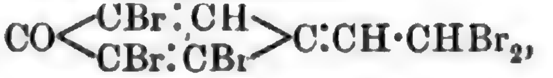
ββ-2 : 3 : 5-Pentabromo-p-ethylidenequinone,



$$CO{<}\begin{matrix}CBr{:}CH\\CBr{:}CBr\end{matrix}{>}C{:}CH{\cdot}CHBr_2,$$

obtained from the hexabromide, is a yellow, granular powder, sintering at 100° and decomposing at 180°; it is accompanied by a white, insoluble product into which it is readily converted by the action of solvents. The quinone readily forms addition products, and with aqueous acetone, methyl alcohol, and acetic acid gives rise to the corresponding α-hydroxy-, α-methoxy-, and α-acetoxy-derivatives of ββ-2 : 3 : 5-pentabromo-*p*-ethylphenol. Hydrogen bromide alone regenerates the hexabromide and in the presence of zinc, β-2 : 3 : 5-tetrabromo-*p*-vinylphenol is produced. The insoluble quinonoid compound also forms the same additive products with hydrogen bromide and methyl alcohol. With aqueous acetone and acetic acid, it yields *compounds* melting respectively at 135—136° and 134—135°; the former has the same composition as the quinone, namely, $C_8H_3Br_5O$, but dissolves in alkali hydroxide solutions, the latter is insoluble in these reagents.

*β-2 : 3 : 5-Tetrabromo-*p*-ethylidenequinone*,



$$CO{<}\begin{matrix}CBr{:}CH\\CBr{:}CBr\end{matrix}{>}C{:}CH{\cdot}CHBr_2,$$

obtained from the pentabromide only in very small amount, is a yellow, amorphous powder; it is accompanied by a large quantity of white, insoluble product. The quinone reacts with hydrogen bromide, regenerating the pentabromide, and when treated with methyl alcohol and acetic acid furnishes the corresponding α-methoxy- and α-acetoxy-derivatives of β-2 : 3 : 5-tetrabromo-*p*-ethylphenol. G. T. M.

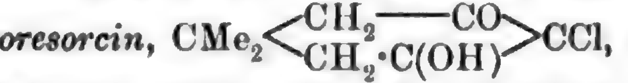
Synthesis of Unsaturated Phenol-Ethers. By August Klages (*Ber.*, 1902, **35**, 2262—2267).—Propionylanisole (Gattermann, Erhardt, and Maisch, Abstr., 1890, 963) which can be prepared in quantity by the action of aluminium chloride on propionyl chloride and anisole, boils at 148° under 14 mm. pressure, and solidifies to colourless crystals. 4-*Methoxy*-1-*α-hydroxypropylbenzene*, $OMe{\cdot}C_6H_4{\cdot}CHEt{\cdot}OH$, is a colourless, viscous oil, boils at 141—142° under 16 mm. pressure and has a sp. gr. 1·042 at 17°. The *phenylurethane* $C_{17}H_{19}O_3N$, crystallises from a mixture of alcohol and light petroleum in stout tablets and melts at 74°. The *acetate*, $C_{12}H_{16}O_3$, boils at 156° under 20 mm. pressure and has a sp. gr. 1·005 at 16°. By heating with pyridine, the acetate was converted into anethole (4-methoxy-1-allylbenzene),

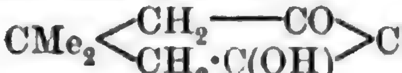
$$OMe{\cdot}C_6H_4{\cdot}CH{:}CHMe.$$

Propionylphenetole, $OEt{\cdot}C_6H_4{\cdot}COEt$, boils at 153—154° under 13 mm. pressure and solidifies on cooling. 4-*Ethoxy*-1-*α-hydroxypropylbenzene*, $OEt{\cdot}C_6H_4{\cdot}CHEt{\cdot}OH$, is a colourless, viscous oil, of a sweet, burning taste, slightly soluble in water, boils at 144·5—145·5° under 10 mm. and at 150° under 15 mm. pressure, and has a sp. gr. 1·0222 at 22°/4°. The *phenylurethane*, $C_{18}H_{21}O_3N$, forms minute, felted needles, and melts at 82°. The *acetate*, $C_{13}H_{18}O_3$, is a water-white, odourless liquid and boils at 161° under 17 mm. pressure. *Anæthole* (*4-ethoxy-1-allylbenzene*), $\mathrm{OEt\cdot C_6H_4\cdot CH{:}CHMe}$, crystallises from alcohol in colourless glistening flakes, is volatile with steam, and boils at 134—136° under 18 mm. and at 242° under atmospheric pressure. The *nitrosochloride*, $\mathrm{C_{11}H_{14}O,ONCl}$, separates in colourless, glistening crystals and melts at 115·5°.

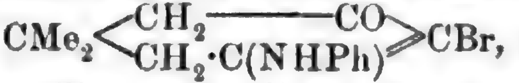
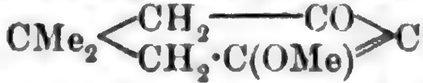
p-*Propionyl*iso*butoxybenzene*, $\mathrm{C_4H_9\cdot O\cdot C_6H_4\cdot COEt}$, crystallises from alcohol in glistening tablets, melts at 52°, and boils at 172—174° under 14 mm. pressure. The *oxime*, $\mathrm{C_{13}H_{19}O_2N}$, separates from absolute alcohol in colourless crystals and melts at 49°. 4-iso*Butoxy-1-a-hydroxypropylbenzene*, $\mathrm{C_4H_9\cdot O\cdot C_6H_4\cdot CHEt\cdot OH}$, is a colourless, oily liquid of faint odour and burning taste and boils at 164—165° under 14 mm. pressure. The *phenylurethane*, $\mathrm{C_{20}H_{25}O_3N}$, separates from alcohol in colourless needles and melts at 57°.

Butyrylphenetole, $\mathrm{OEt\cdot C_6H_4\cdot COPr^a}$, boils at 173—174° under 23 mm. pressure, has a faint odour, and solidifies to colourless crystals. 4-*Ethoxy-1-a-hydroxybutylbenzene*, $\mathrm{OEt\cdot C_6H_4\cdot CHPr^a\cdot OH}$, boils at 164—166° under 23 mm. pressure, melts at about 22°, and has a sp. gr. 1·003 at 19°. *Butenylphenetole*, $\mathrm{OEt\cdot C_6H_4\cdot CH{:}CHEt}$, is a colourless oil of pleasant aromatic odour, boils at 123—124° under 12 mm. pressure and has a sp. gr. 0·9452 at 20°. T. M. L.

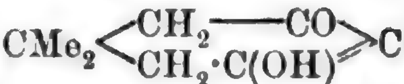
Halogen Derivatives of Dimethyldihydroresorcin. By DANIEL VORLÄNDER and M. KOHLMANN (*Annalen*, 1902, **322**, 239—259. Compare Crossley and Le Sueur, Trans., 1902, **81**, 821).—*Chlorodimethyldihydroresorcin*,  $\mathrm{CMe_2}\Big<\begin{array}{l}\mathrm{CH_2—CO}\\ \mathrm{CH_2\cdot C(OH)}\end{array}\Big>\mathrm{CCl}$, produced together with dimethylglutaric acid by the action of alkali hypochlorites on dimethyldihydroresorcin, crystallises from alcohol in leaflets containing $\mathrm{1H_2O}$. The water of crystallisation is removed by leaving the substance in a desiccator; the anhydrous compound melts at 161°.

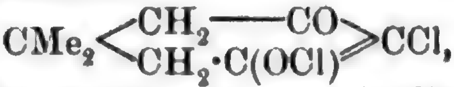
Bromodimethyldihydroresorcin,  $\mathrm{CMe_2}\Big<\begin{array}{l}\mathrm{CH_2—CO}\\ \mathrm{CH_2\cdot C(OH)}\end{array}\Big>\mathrm{CBr}$, prepared by treating dimethyldihydroresorcin either with bromine dissolved in chloroform or an alkaline solution of a hypobromite, crystallises in leaflets also containing $\mathrm{1H_2O}$; the anhydrous substance melts at 175° and not at 143—144°. This compound, when treated with excess of hypobromite, is oxidised, yielding a mixture of carbon tetrabromide and ββ-dimethylglutaric acid.

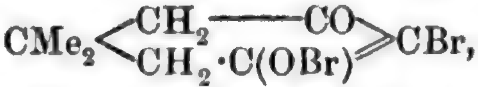
These two monohalogen derivatives behave as monobasic acids.

The *anilide*,  $\mathrm{CMe_2}\Big<\begin{array}{l}\mathrm{CH_2——CO}\\ \mathrm{CH_2\cdot C(NHPh)}\end{array}\Big>\mathrm{CBr}$, produced by heating this substance with aniline, crystallises from glacial acetic acid and melts at 159—160°. The *methyl* ester,  $\mathrm{CMe_2}\Big<\begin{array}{l}\mathrm{CH_2——CO}\\ \mathrm{CH_2\cdot C(OMe)}\end{array}\Big>\mathrm{CBr}$, obtained by boiling the hydroxy-compound with methyl alcohol containing sulphuric acid, crystallises from methyl alcohol and melts at 104°.

The *methyl* ester of dimethyldihydroresorcin, prepared in a similar manner, is a colourless oil boiling at 132—134° under 15 mm. pressure; when treated with bromine in chloroform solution, it yields bromodimethyldihydroresorcinol and a white, indeterminate substance.

Iododimethyldihydroresorcin,  $CMe_2\begin{matrix}<CH_2\text{——}CO>\\<CH_2\cdot C(OH)\geqslant\end{matrix}CI$, produced by mixing an ethereal solution of iodine with an alcoholic solution of the sodium derivative of dimethyldihydroresorcin, crystallises from dilute methyl alcohol in slender needles partially decomposing at 135° and melting at 160—162°. These halogen derivatives of dimethyldihydroresorcin are very stable towards boiling sodium hydroxide solutions, the chloro- and bromo-compounds remain practically unchanged, whilst the iodo-derivative is only slightly attacked.

Dichlorodimethyldihydroresorcin,  $CMe_2\begin{matrix}<CH_2\text{——}CO>\\<CH_2\cdot C(OCl)\geqslant\end{matrix}CCl$, results from the action of dry chlorine on dimethyldihydroresorcin dissolved in chloroform, crystallises in lustrous needles and melts at 112°; it dissolves in the ordinary organic solvents, but is insoluble in cold solutions of alkali hydroxides; when, however, the mixture is warmed, the dichloride is decomposed, and the solution then contains an alkali hypochlorite. Stannous chloride reduces the dichloride, giving rise to chlorodimethyldihydroresorcin.

Dibromodimethyldihydroresorcin,  $CMe_2\begin{matrix}<CH_2\text{——}CO>\\<CH_2\cdot C(OBr)\geqslant\end{matrix}CBr$, also prepared by the action of the halogen in chloroform solution, crystallises from dilute methyl alcohol in needles melting at 144°. With excess of dimethyldihydroresorcin, this reaction leads to the formation of the monobromide accompanied by tarry products. The dibromide is insoluble in solutions of the alkali carbonates or hydroxides, but when shaken up with the latter it slowly decomposes, and the solution is found to contain bromoform, carbon tetrabromide, and an alkali hypobromite; this reaction occurs more rapidly on warming.

These disubstituted halogen derivatives both liberate iodine from a solution of potassium iodide; this action does not occur with the monohalogen compounds.

$\beta\beta$-Dimethylglutaric acid can be very readily prepared by treating an alkaline solution of dimethyldihydroresorcin at 40—50° with an emulsion of chloride of lime. G. T. M.

Styrene. By August Klages [in part with Emil Fanto and Hermann Pierstorff] (*Ber.*, 1902, **35**, 2245—2262).—1-*Methyl*-4-a-*hydroxyethylbenzene*, $C_6H_4Me\cdot CHMe\cdot OH$, prepared by reducing *p*-acetyltoluene with sodium and ethyl alcohol, is a colourless, viscous oil, boils at 120° under 19 mm. pressure, and has a sp. gr. 0·9668 at 15·5°/4°. The *phenylurethane*, $C_{16}H_{17}O_2N$, is a crystalline compound, melts at 95—96°, and dissolves readily in benzene. The *chloride*, $C_6H_4Me\cdot CHMeCl$, is a pale, yellowish oil which liberates hydrogen chloride when heated. *p*-Methylstyrene, $C_6H_4Me\cdot CH{:}CH_2$, prepared by heating the chloride with pyridine, is a colourless, mobile oil with an odour suggestive of turpentine, boils at 60° under 12 mm. pressure, and has a sp. gr. 0·8974 at 18°/4°. A nitrosochloride could not be obtained.

1 : 3-*Dimethyl*-4-a-*hydroxyethylbenzene*, $C_6H_3Me_2\cdot CHMe\cdot OH$, is a colourless, viscous oil of sharp odour, boils at 118° under 12 mm. pressure, and has a sp. gr. 0·9863 at 13°/4°. The *phenylurethane*, $C_{17}H_{19}O_2N$, separates from light petroleum in colourless needles and

melts at 105°. The *chloride* forms an additive product, $C_{15}H_{18}NCl,H_2O$, with pyridine, which separates in needles from a mixture of alcohol and ether and melts at 153°; the *platinichloride*, $(C_{15}H_{17}N)_2,H_2PtCl_6$, separates from hot water in yellowish needles and melts at 198°; the *aurichloride*, $C_{15}H_{17}N,HAuCl_4$, crystallises from alcohol in well-formed, golden-yellow needles, melts at 113°, and is more soluble than the platinichloride. When heated with water at 100°, the additive product decomposes into pyridine hydrochloride and dimethylstyrene, but when heated with water at 120° it gives a polymeride, $(C_{10}H_{12})_8$, resembling Canada balsam.

The *oxime* of p-*acetyl ethylbenzene* (Klages and Lickroth, Abstr., 1899, i, 599) crystallises from alcohol in stout, tabular crystals and melts at 82—83°.

1-*Ethyl-4-α-hydroxyethylbenzene*, $C_6H_4Et{\cdot}CHMe{\cdot}OH$, is a colourless, viscous oil with a faint odour, boils at 119·5° under 14 mm. pressure, and has a sp. gr. 0·9737 at 18°/4°. The *phenylurethane*, $C_{17}H_{19}O_2N$, crystallises from alcohol in needles and melts at 72—73°. The *chloride*, $C_6H_4Et{\cdot}CHMeCl$, is a colourless, mobile oil and boils at 112·5—113° under 18 mm. pressure. p-*Ethylstyrene*, $C_6H_4Et{\cdot}CH{:}CH_2$, is a colourless, mobile oil with an odour suggestive of turpentine, boils at 86° under 20 mm. pressure, and has a sp. gr. 0·9074 at 13°/4°; after some weeks, it changes to an odourless, stiff, transparent resin; a nitrosochloride could not be obtained.

Vinylmesitylene (2 : 4 : 6-trimethylstyrene) (Klages and Allendorff, Abstr., 1898, i, 433) can be prepared by a similar method; it does not polymerise after keeping for a year, and does not yield a nitrosochloride.

Allylbenzene, $C_6H_5{\cdot}CH{:}CHMe$, boils at 74° under 13 mm. pressure and has a sp. gr. 0·9083 at 19°/4°.

1-*Methyl-4-α-hydroxypropylbenzene*, $C_6H_4Me{\cdot}CHEt{\cdot}OH$, boils at 118—120° under 23 mm., and at 223—226° under atmospheric pressure, has a sp. gr. 0·966 at 14·5°, and solidifies on ice to colourless crystals melting at 15°. The *acetate*, $C_{12}H_{16}O_2$, boils at 130° under 25 mm. pressure and has a sp. gr. 0·989 at 14°. The *phenylurethane*, $C_{17}H_{19}O_2N$, separates from light petroleum in colourless crystals and melts at 86—88°. The *chloride*, $C_6H_4Me{\cdot}CHEt{\cdot}Cl$, is largely decomposed with liberation of hydrogen chloride when distilled in a vacuum. *p*-Methylallylbenzene, $C_6H_4Me{\cdot}CH{:}CHMe$, is a colourless, mobile oil with an odour resembling that of styrene, and boils at 92—93° under 20 mm. pressure. The *nitrosochloride*, $C_{10}H_{12}ONCl$, is readily formed and is very characteristic. It separates in colourless needles and melts at 135°. The hydrocarbon is perhaps identical with Errera's allyltoluene (Abstr., 1885, 772).

Propionylmesitylene, $C_6H_2Me_3{\cdot}COEt$, is a yellowish, mobile liquid of sharp odour, boils at 125° under 13 mm. pressure, and has the sp. gr. 0·962 at 24°/4°. 1 : 3 : 5-*Trimethyl-2-α-hydroxypropylbenzene*,

$$C_6H_2Me_3{\cdot}CHEt{\cdot}OH,$$

is a viscous, colourless oil, boils at 172° under 14 mm. pressure, and has a sp. gr. 0·9705 at 24°/4°. The *phenylurethane*, $C_{19}H_{23}O_2N$, crystallises from alcohol in colourless needles and melts at 141°. The *chloride* was converted directly, by boiling with pyridine, into *allylmesitylene*, $C_6H_2Me_3{\cdot}CH{:}CHMe$, a colourless, mobile liquid of turpentine-like odour, which boils at 103° under 13 mm. pressure, has a sp. gr. 0·9003 at 17·5°/4°, and does not polymerise on keeping. The *nitrosochloride*, $C_{12}H_{16}ONCl$, separates in minute crystals and melts at 146·5°.

4-Butyryl-1 : 3-dimethylbenzene, $C_6H_3Me_2{\cdot}COPr^a$, is a colourless, mobile oil, boils at 135° under 17 mm. pressure, and has a sp. gr. 0·9691 at 21·5°/4°.

1 : 3-*Dimethyl-4-a-hydroxybutylbenzene*, $C_6H_3Me_2{\cdot}CHPr^a{\cdot}OH$, is a colourless, mobile oil, boils at 134° under 14 mm. pressure, and has a sp. gr. 0·9611 at 13°/4°. The *chloride*, $C_6H_3Me_2{\cdot}CHPr^aCl$, boils at 129° under 14 mm. pressure.

p-*Butenyl*-m-*xylene*, $C_6H_3Me_2{\cdot}CH{:}CHEt$, is a colourless, mobile liquid, boils at 114° under 21 mm. pressure, has a sp. gr. 0·8937 at 19°/4°, and has an odour suggestive of almonds. The *nitrosochloride*, $C_{12}H_{16}ONCl$, separates in white needles and melts at 135°.

Butyrylmesitylene, $C_6H_2Me_3{\cdot}COPr^a$, is a pale yellowish oil, boils at 140° under 14 mm. pressure, and yields mesitylene when heated with hydriodic acid.

1 : 3 : 5-*Trimethyl-2-a-hydroxybutylbenzene*, $C_6H_2Me_3{\cdot}CHPr^a{\cdot}OH$, is a colourless, somewhat viscous oil, boils at 147·5° under 12 mm. pressure, and has a sp. gr. 0·964 at 17°/4°, and when heated with hydriodic acid it yields, not mesitylene, but *n*-butylmesitylene. The *phenylurethane*, $C_{20}H_{25}O_2N$, is prepared with difficulty, and was separated from large quantities of diphenylcarbamide by extracting with benzene; it crystallises from alcohol in white needles and melts at 119—120°. The *acetate*, $C_{15}H_{22}O_2$, is a colourless liquid, boils at 140—141° under 9 mm. pressure, and has a sp. gr. 0·976 at 14·5°/4°. *Butenylmesitylene*, $C_6H_2Me_3{\cdot}CH{:}CHEt$, is a colourless, mobile oil, boils at 118—119° under 14 mm. pressure, and has a sp. gr. 0·8953 at 14°/4°. The *nitrosochloride*, $C_{13}H_{18}ONCl$, separates in colourless crystals and melts at 122—122·5°.

m-*Xylyl pentadecyl ketone*, $C_6H_3Me_2{\cdot}CO{\cdot}C_{15}H_{31}$, from palmityl chloride and *m*-xylene, boils at 259° under 11 mm. pressure, and melts at 35°.

1 : 3-*Dimethyl-4-a-hydroxyhexadecylbenzene*, $C_6H_3Me_2{\cdot}CH(OH){\cdot}C_{15}H_{31}$, crystallises in white, fatty flakes, melts at 23—24°, and boils at 267° under 20 mm. pressure. *Hexadecenyl*-m-*xylene*, $C_6H_3Me_2{\cdot}CH{:}CH{\cdot}C_{14}H_{29}$, is a colourless, viscous oil, boils at 254° under 17 mm. pressure, and has a sp. gr. 0·868 at 20°/4°.

Mesityl pentadecyl ketone, $C_6H_2Me_3{\cdot}CO{\cdot}C_{15}H_{31}$, separates from alcohol in crystalline aggregates or glistening flakes with a fatty feeling, boils at 262° under 13 mm. pressure, and melts at 41°. 1 : 3 : 5-*Trimethyl-2-a-hydroxyhexadecylbenzene*, $C_6H_2Me_3{\cdot}CH(OH){\cdot}C_{15}H_{31}$, crystallises from alcohol in needles, boils at 274° under 16 mm. pressure, and melts at 47·5°. The *chloride* is a thick, yellowish oil.

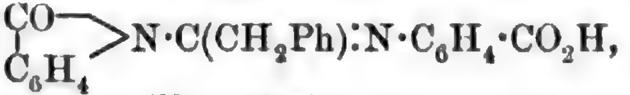
Hexadecenylmesitylene, $C_6H_2Me_3{\cdot}CH{:}CH{\cdot}C_{14}H_{29}$, forms long needles, melts at 28·5—29°, boils at 260° under 23 mm. pressure, and has no appreciable tendency to polymerise. T. M. L.

Separation of Phenylalanine from Amino-acids. By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1902, **35**, 210—226).—The authors find that the isolation of phenylalanine by means of its copper derivative as suggested by Schulze and Barbieri

(Abstr., 1883, 1122), is accompanied with loss of material in the presence of aminovaleric acid and fails entirely in the presence of a large proportion of leucine such as occurs in the hydrolytic products of conglutin.

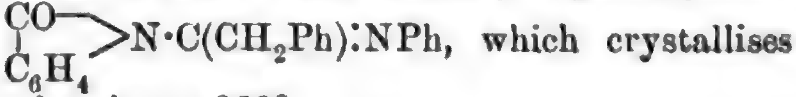
Mercuric nitrate is found to precipitate phenylalanine incompletly in presence of leucine and a better separation is secured by the subsequent addition of sodium carbonate. Phosphotungstic acid precipitates phenylalanine from solutions containing 0·25 per cent. of this substance alone, and from more concentrated solutions even in presence of other amino-acids, the separation in both cases being improved by the addition of a small quantity of sulphuric acid. With the aid of this reagent, phenylalanine has been isolated from etiolated seedlings of *Lupinus albus* and *Vicia sativa*, and from the products of alkaline hydrolysis of conglutin and of the proteid of pumpkin seeds. This method of isolation does not interfere with the eventual separation of other amino-acids which may be present. The phosphotungstic compound is soluble in boiling water, slightly so in cold (72 per cent. at 15—16°), and readily in alcohol; it crystallises from hot water in silky leaflets, from which the amino-acid is regenerated in a pure state by addition of excess of baryta water, the latter being in turn removed by carbon dioxide. T. A. H.

Amidine Derivatives of Anthranilic Anhydride. By STEFAN VON NIEMENTOWSKI (*Bull. Acad. Sci. Cracow*, 1902, 232—234).—*Phenylethenyldianthranilic anhydride*,

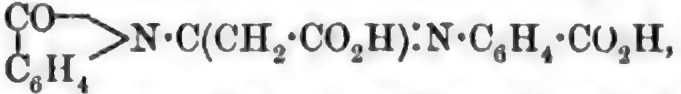


$$\left.\begin{matrix}CO\\|\\C_6H_4\end{matrix}\right>N\cdot C(CH_2Ph):N\cdot C_6H_4\cdot CO_2H,$$

formed by boiling anthranilic acid with phenylacetic acid or its ethyl ester for several days, crystallises in long, greenish-yellow leaflets, is soluble with difficulty in benzene or alcohol, more easily in acetone or ethyl acetate, and melts at 283°. The *platinichloride*, $(C_{22}H_{16}O_3N_2)_2,H_2PtCl_6$, melts and decomposes at 256—258°. Prolonged boiling in alkaline solution results in the formation of *phenylethenyldianthranilic acid*, which crystallises in small, colourless prisms and melts and effervesces at 190°. The silver salt, $C_{22}H_{16}O_4N_2Ag_2$, forms a white precipitate, very sensitive to light.

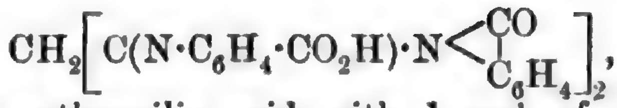
When the anhydride is heated with concentrated hydrochloric acid at 210°, it loses 1 mol. of carbon dioxide and forms *phenylethenylanilanthranilic anhydride*,  $\left.\begin{matrix}CO\\|\\C_6H_4\end{matrix}\right>N\cdot C(CH_2Ph):NPh$, which crystallises in white, silky needles and melts at 229°.

The *anhydride* of methenyldianthranilacetic acid,



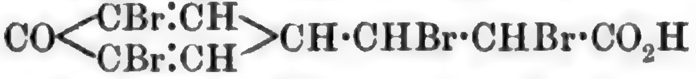
$$\left.\begin{matrix}CO\\|\\C_6H_4\end{matrix}\right>N\cdot C(CH_2\cdot CO_2H):N\cdot C_6H_4\cdot CO_2H,$$

obtained by heating 2 mols. of anthranilic acid with 1 mol. of ethyl malonate, is insoluble or only slightly soluble in all solvents, crystallises in microscopic plates, melts and decomposes at 302°, and, when heated in alkaline solution, is hydrolysed to *methenyldianthranilacetic acid*, which is easily soluble in organic solvents or hot water, crystallises in thin, small prisms, and melts and effervesces at 190°. *Malon-*

tetranthranilic dianhydride,  $\mathrm{CH_2}\left[\mathrm{C(N{\cdot}C_6H_4{\cdot}CO_2H){\cdot}N}{<}\begin{matrix}\mathrm{CO}\\ |\\ \mathrm{C_6H_4}\end{matrix}\right]_2$, obtained by heating 4 mols. of anthranilic acid with 1 mol. of ethyl malonate, is soluble with difficulty in acetic acid, easily in phenylhydrazine, crystallises in yellow needles, melts and effervesces at 275°, and is hydrolysed by boiling aqueous alkalis to *malontetranilic acid*, which crystallises in white needles, is soluble with difficulty in organic solvents, easily soluble in alkalis, insoluble in dilute acids, and melts and decomposes at 263—265°. G. Y.

Action of Bromine on *p*-Hydroxycinnamic Acid; Tetrabromo-*p*-hydroxycinnamic Acid. Brominated *p*-Vinyl- and *p*-Ethyl-phenol Derivatives. By THEODOR ZINCKE and FR. LEISSE (*Annalen*, 1902, **322**, 220—238. Compare this vol., i, 605).—*p*-Hydroxycinnamic acid yields a *methyl* ester crystallising in white needles melting at 137°.

αβ-3 : 5-Tetrabromo-β-4-hydroxyphenylpropionic acid,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CH}\end{matrix}{>}\mathrm{CH{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H}$$

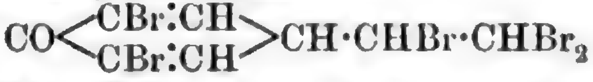
or $\mathrm{OH{\cdot}C_6H_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2H}$, obtained by heating *p*-hydroxycinnamic acid with bromine on the water-bath, crystallises from glacial acetic acid in white needles melting at 191°; when treated with hydriodic acid, it yields 3 : 5-dibromo-β-4-hydroxyphenylpropionic acid melting at 114°, and not at 107—108° (compare Stöhr, Abstr., 1884, 1349); the *methyl* ester of this product crystallises in white needles melting at 55°.

Methyl α-3 : 5-tribromo-β-methoxy-β-4-hydroxyphenylpropionate, $\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CH(OMe){\cdot}CHBr{\cdot}CO_2Me}$, produced by heating the tetrabromo-acid with alcohol and hydrogen chloride, crystallises from this solvent in white needles melting at 142°; its *acetyl* derivative forms short, white needles and melts at 142°.

α-3 : 5-Tribromo-β-methoxy-β-4-hydroxyphenylpropionic acid, $\mathrm{OH{\cdot}CH_2Br_2{\cdot}CH(OEt){\cdot}CHBr{\cdot}CO_2H}$, obtained by boiling the tetrabromo-acid with ethyl alcohol, crystallises in lustrous white needles and melts at 174°; its methyl ester is oily, but yields an *acetyl* derivative crystallising in white leaflets and melting at 119°.

β-3 :5-Tribromo-p-vinylphenol, $\mathrm{OH{\cdot}C_6H_2Br{\cdot}CH{:}CHBr}$, produced by the action of alcoholic potassium hydroxide on the tetrabromo-acid, crystallises in lustrous, white needles and melts at 110°; the *acetyl* derivative forms white needles melting at 124°.

αββ-3 : 5-Pentabromo-ψ-p-ethylphenol,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CH}\end{matrix}{>}\mathrm{CH{\cdot}CHBr{\cdot}CHBr_2}$$

or $\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CHBr{\cdot}CHBr_2}$, is readily prepared by adding bromine to the preceding compound, and was once obtained by the direct action of the halogen on *p*-ethylphenol; it crystallises in needles or prisms and melts at 106—107°.

ββ-3 : 5-Tetrabromo-α-hydroxy-p-ethylphenol,

$$\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CH(OH){\cdot}CHBr_2},$$

produced by warming the preceding compound with dilute acetone, crystallises from a mixture of benzene and petroleum in needles melting at

147—148°; its diacetyl compound forms colourless prisms and melts at 103°. The *methoxy*-derivative, $\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CH(OMe){\cdot}CHBr_2}$, prepared by the action of methyl alcohol, separates in colourless needles and melts at 72°.

*aβ-3 : 5-Tetrabromo-ψ-*p*-ethylphenol,*

$$\mathrm{CO}\Big<\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CH}\end{matrix}\Big>\mathrm{CH{\cdot}CHBr{\cdot}CH_2Br}$$

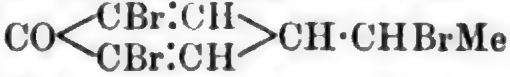
or $\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CHBr{\cdot}CH_2Br}$, is readily prepared by adding hydrogen bromide to the preceding vinyl compound, and was also once obtained from *p*-ethylphenol; it crystallises from light petroleum in colourless needles melting at 123°. This substance is readily converted by reduction into 3 : *5-dibromo-*p*-vinylphenol*, a compound crystallising in leaflets and melting at 73—74°.

*β-3 : 5-Tribromo-a-hydroxy-*p*-ethylphenol,*

$$\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CH(OH){\cdot}CH_2Br},$$

produced by the action of dilute acetone on the preceding tetrabromo-compound, separates in monoclinic prisms and melts at 107°; its diacetyl derivative melts at 103°. The corresponding *methyl* compound, $\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CH(OMe){\cdot}CH_2Br}$, crystallises in needles melting at 112°, and the *ethyl* derivative forms white plates melting at 86°.

3 : 5-Dibromo-*p*-vinylphenol yields an *acetyl* derivative crystallising in white leaflets and melting at 76—77°; it also gives rise to an oily tribromo-derivative, *aβ-dibromo-*p*-ethyl-3 : 5-ψ-phenol,*



$$\mathrm{CO}\Big<\begin{matrix}\mathrm{CBr{:}CH}\\ \mathrm{CBr{:}CH}\end{matrix}\Big>\mathrm{CH{\cdot}CHBrMe}$$

or $\mathrm{OH{\cdot}C_6H_2Br{\cdot}CHMeBr}$, on treatment with hydrogen bromide; this product, when warmed with dilute acetic acid, furnishes 3 : *5-dibromo-a-hydroxy-*p*-ethylphenol*, $\mathrm{OH{\cdot}C_6H_2Br_2{\cdot}CHMe{\cdot}OH}$, which crystallises in rectangular plates and melts at 149°; its *diacetyl* derivative separates in needles melting at 55—56°. The *a-methyl* derivative crystallises in hard needles and melts at 100—101°, whilst the a-ethyl compound forms thick, prismatic crystals and melts at 99—100°. G. T. M.

Colouring Matters obtainable by the Action of Isatin on Extracts of Isatis Tinctoria. By LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 227—230).—Results identical with Beyerinck's (Abstr., 1900, i, 230, 649) are obtained by treating the fresh leaves of *Isatis tinctoria* with boiling water, but on extracting the dried leaves with alcohol a substance is obtained which, on treatment with isatin in aqueous solution, yields a colouring matter, *isatocyanin*, a blackish-brown powder which dissolves easily in glacial acetic acid and sparingly in alcohol to blue solutions which become colourless on keeping; it dissolves in boiling phenol and is reprecipitated by ether; in concentrated sulphuric acid, it forms a yellow solution which becomes blue on keeping. The absorption spectrum shows a band with maximum intensity at the sodium line. Isatocyanin resembles but is not identical with the colouring matters obtained by the action of pyrroline on isatin, and of acetic anhydride on the condensation product of piperidine and isatin. The spectrum of the former shows general absorption of the red, of the latter, a band with maxium intensity at λ 618—661. G. Y.

Synthesis of α-Truxillic Acid. By C. N. Riiber (*Ber.*, 1902, **35**, 2411—2415).—Molecular weight determinations from the boiling point of solutions in acetone have shown that Liebermann's white cinnamylidene-malonic acid (Abstr., 1895, i, 470) is a bimolecular compound. When oxidised with alkaline permanganate, it yields Liebermann's α-truxillic acid (Abstr., 1889 1194 ; 1890, 1424) identical with that found with the cocaine alkaloids ; the bimolecular acid has therefore the constitution $\mathrm{C(CO_2H)_2{:}CH{\cdot}CH}<\begin{array}{c}\mathrm{CHPh}\\ \mathrm{CHPh}\end{array}>\mathrm{CH{:}C(CO_2H)_2}$. When distilled in an absolute vacuum, it loses carbon dioxide and leaves an *acid*, $C_{22}H_{20}O_3$, isomeric with the two known cinnamylidene-acetic acids ; this separates from dilute alcohol in microscopic needles and melts at 204°. α-Truxillic acid sublimes unchanged in an absolute vacuum. T. M. L.

Esterification of Unsymmetrical Di- and Poly-basic Acids. IV. Conductivity of some Acids and Acid Esters. By Rudolf Wegscheider (*Monatsh.*, 1902, **23**, 317—356. Compare Abstr., 1901, i, 32).—3-Nitrophthalic acid commences to show dibasic dissociation at the dilution $v = 514$, and has a conductivity K 1·31 (compare Ostwald, Abstr., 1889, 818). A specimen of the α-monomethyl ester, previously found to melt at 142°, now melts at 146—149°. It is probable that this ester occurs in two forms, the labile form melting at 144°, the stable form at 152—153° (compare McKenzie, Trans., 1901, **79**, 1141). The β-monomethyl ester $[CO_2Me : CO_2H : NO_2 = 1 : 2 : 3]$ is now found to have the conductivity K 1·6

4-Nitrophthalic acid commences to show dibasic dissociation at the dilution $v = 256$, but does not do so strongly until $v = 1024$. The author considers his value, K 0·77, as probably more correct than Ostwald's (*loc. cit.*). The monomethyl ester has a conductivity K 0·46. 4-Hydroxyphthalic acid does not show dibasic dissociation at the dilution $v = 1033$; it has a conductivity K 0·12. Only one *monomethyl ester* could be obtained ; it melts at 166°, and has a conductivity K 0·0205. The *dimethyl ester* has a conductivity K 10^{-5} (?), resembling *para*- and *meta*-nitrophenol.

3 : 6-Dichlorophthalic acid commences to show dibasic dissociation at a slightly greater dilution than $v = 51$, it has a conductivity K 3·45. The monomethyl ester is easily hydrolysed by warm water ; it has a conductivity K 1·5. Kirpal's conductivity constant, K 0·11, for hemipinic acid (Abstr., 1898, i, 87) is confirmed. That the value of K for hemipinic acid is lower than for *m*-hemipinic acid, shows that the multiplication of substituting groups leads occasionally to abnormal results. *n*-Propyl hydrogen hemipinate has a conductivity K 0·0144, the β-acid ester has K 0·093. Bromoterephthalic acid shows dibasic dissociation at dilutions over $v = 255$; it has a conductivity K 0·62. The α-monomethyl ester has most probably the constitution $[CO_2H : Br : CO_2Me = 1 : 3 : 4]$, and the corresponding β ester (m. p. 164°) $[CO_2H : Br : CO_2Me = 1 : 2 : 4]$ (compare Abstr., 1900, i, 658).

Nitroterephthalic acid shows dibasic dissociation at dilutions greater than $v = 32$; it has a conductivity K 1·87. The *α-monomethyl ester*

[$CO_2H : NO_2 : CO_2Me = 1 : 3 : 4$], melts at 174—175·5°, and has a conductivity *K* 0·0770. The *β-monomethyl ester* [$CO_2H : NO_2 : CO_2Me = 1 : 2 : 4$] melts at 133—134°, and has a conductivity *K* 1·90.

Hydroxyterephthalic acid shows dibasic dissociation at the dilution $v = 200$; it has a conductivity *K* 0·269. The α-monomethyl ester has a conductivity *K* 0·025; the β-ester resembles salicylic acid in its ferric chloride reaction and its solubility in chloroform, it has a conductivity *K* 0·277.

The β-monomethyl ester of papaveric acid is easily hydrolysed by water; the most accurate conductivity constant, *K* 0·39, is probably correct to ± 20 per cent., the same accuracy is obtained for the conductivity *K* 0·61 of the γ-monomethyl ester. These results agree with the formulæ proposed by Goldschmiedt and Kirpal for these methyl esters (Abstr., 1897, i, 131).

m-Sulphobenzoic acid follows Ostwald's law of dilution to $v = 90$; at $v = 180$ it shows dibasic dissociation, and has the conductivity *K* 40 (?), van't Hoff's dissociation constant *k* rises from *k* 1·69 at $v = 11·27$ to *k* 4·66 at $v = 90·6$. It is shown by calculations from the conductivity of benzenesulphonic acid that the behaviour of *k* depends on the value chosen for $\mu\infty$. With $\mu\infty = 360$, *k* rises from 1·61 at $v = 32$ to 7·77 at $v = 1024$, whereas with $\mu\infty = 366$, *k* remains approximately constant.

It would seem as if variations from Ostwald's law of dilution depend on the nature as well as on the concentration of the ions. *α-Methyl hydrogen* m*-sulphobenzoate* [$CO_2H : SO_3Me$] melts at 138°, is easily hydrolysed by water, and has a conductivity *K* 0·068. The β-monomethyl ester [$CO_2Me : SO_3H$], is very soluble in water and has a conductivity *K* 20 (?). Tribromobenzoic acid has a conductivity *K* 3·90.

Applying the formula $K_\alpha + K_\beta = aK$ (Abstr., 1895, ii, 310) to the present results, greater variations are found in the factor *a* (mean value $a = 0·90$). It is apparent that the stronger the dibasic acid the smaller the dilution at which dibasic dissociation becomes marked.

G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids. V. Constitution of some Acid Esters. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1902, **23**, 357—368. Compare foregoing abstract).—The conductivity of methyl hydrogen 4-hydroxyphthalate agrees with that calculated for the α-acid ester [$CO_2H : CO_2Me : OH = 1 : 2 : 4$]. The calculated conductivities of the α- and β-monomethyl esters of 4-nitrophthalic acid are too close to admit of any conclusion as to the constitution of the acid ester formed.

The conductivities of the *ortho-* and *allo-*methyl hydrogen camphorates agree with different formulæ proposed by Bouveault, Bredt, Perkin, and Schryver, but not with those proposed by Tiemann and Wagner.

The conductivities of α- and β-monomethyl esters of tricarballylic acid (Bone and Sprankling, Trans., 1902, **81**, 34) do not agree with those calculated. The affinity constant of the monomethyl ester of αα-dimethyltricarballylic acid, obtained by hydrolysis of the trimethyl ester, agrees with the formula $CO_2H{\cdot}CMe_2{\cdot}CH(CO_2Me){\cdot}CH_2{\cdot}CO_2H$. The ester obtained by direct esterification agrees in its conductivity with the formula $CO_2H{\cdot}CMe_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2Me$. G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids. VI. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1902, **23**, 369—392).—Methyl opianate (m. p. 81—84°) gives with *m*-phenylenediamine hydrochloride in aqueous or alcoholic solution a light yellow colour which becomes darker on standing (Abstr., 1897, ii, 468), giving evidence of the presence of an aldehyde group. ψ-Methyl opianate gives no reaction.

Treatment of ψ-methyl opianate in absolute ethereal solution with hydrogen peroxide, chromium trioxide, or chloranil does not lead to formation of β-monomethyl hemipinate, except perhaps in traces. Treatment of the ψ-methyl ester with potassium permanganate in acetone solutions leads to the formation of opianic anhydride and a *substance*, $C_{23}H_{22}O_{11}$, which crystallises in large, clear, colourless prisms and melts at 192—194°.

β-Ethyl hydrogen hemipinate is only slightly hydrolysed by cold aqueous or alcoholic ammonia; on heating with alcoholic ammonia at 125°, a trace of hemipinimide is formed.

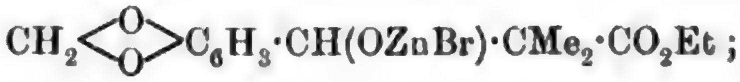
α-Methyl hydrogen hydroxyterephthalate is formed by boiling the potassium hydrogen salt with methyl sulphate in methyl alcohol solution; excess of methyl sulphate leads to the formation of the dimethyl ester. By heating the potassium acid salt with methyl iodide and methyl alcohol at 100°, the β-monomethyl ester is formed (compare Abstr., 1900, i, 658). When hydrolysed by 1 mol. of potassium hydroxide in methyl alcohol solution, dimethyl papaverate yields a mixture of the β- and γ-monomethyl esters, along with a small quantity of free acid. The γ-ester is sparingly soluble in cold methyl alcohol, from which it easily crystallises; the β-ester is easily soluble. When acted on by methyl alcohol, papaveric anhydride forms principally the β-monomethyl ester (m. p. 156—157°), and a small quantity of the γ-monomethyl ester. G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids. VII. Esterification of 4-Hydroxyphthalic Acid. By RUDOLF WEGSCHEIDER and RICHARD PIESEN (*Monatsh.*, 1902, **23**, 393—404).—α-Methyl hydrogen 4-hydroxyphthalate (m. p. 166°) is formed by the action of methyl alcohol on the acid, with or without addition of mineral acids, by partial hydrolysis of the dimethyl ester by potassium hydroxide, by the action of methyl alcohol on the anhydride, and by the action of methyl iodide on the acid potassium salt. The isomeric ester was not obtained by the action of sodium methoxide on the anhydride. The α-monomethyl ester crystallises from water in broad needles and gives a yellow coloration with ferric chloride in aqueous solution. The dimethyl ester is easily formed by the action of methyl alcohol on the acid in presence of hydrogen chloride or sulphuric acid; it dissolves in benzene, is reprecipitated by addition of light petroleum, and melts at 104°. One mol. of the dimethyl ester requires 0·65 mol. of potassium hydroxide for neutralisation; 1 mol. of monomethyl ester requires 1·16 mols. of potassium hydroxide, and 1 mol. of the acid requires 1·94 mols. of potassium hydroxide, the acidity of the phenolic hydroxyl increasing with esterfication of the carboxylic groups. 4-Hydroxyphthalic anhydride is best prepared by heating the acid at 200° in a stream of hydrogen or carbon dioxide. G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids. VIII. Esterification of Nitroterephthalic Acid. II. By RUDOLF WEGSCHEIDER [and, in part, by RICHARD PIESEN and OTTO BREYER] (*Monatsh.*, 1902, **23**, 405—414. Compare Abstr., 1900, i, 657).—On partial hydrolysis by potassium hydroxide or hydrochloric acid, dimethyl-nitroterephthalate yields α-methyl hydrogen nitroterephthalate along with a small quantity of the β-monomethyl ester. The α-acid ester is also formed by the action of methyl iodide on potassium hydrogen nitroterephthalate. It crystallises from water or benzene in microscopic, thick prisms. The β-acid ester is formed by the action of methyl alcohol on the acid in the presence of mineral acids along with the dimethyl ester. It crystallises from benzene in needles which melt at 133—134°, from water in crystals containing $1H_2O$ and melting at 80°. G. Y.

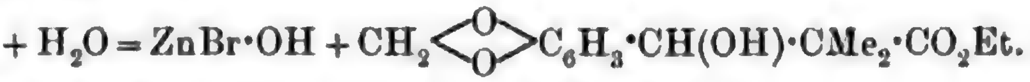
Action of Zinc and Ethyl Bromoisobutyrate on Piperonaldehyde. Synthesis of α-Dimethyl-β-hydroxy-β-piperonylpropionic Acid. By P. MUSCHINSKY (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 370—375).—Reformatsky's method of preparing tertiary hydroxy-acids by the action of a mixture of zinc and a monohaloid ester on a compound containing a carbonyl group, is found to fail when the last-named compound is an aromatic aldehyde containing a hydroxyl group in the benzene nucleus. In order to decide whether the cause of such failure lies in the presence of the hydroxyl group or of non-carbonyl oxygen in general, the author has studied the action of zinc and ethyl bromoisobutyrate on piperonaldehyde, the result indicating that it is the hydroxyl group which prevents the reaction in the above-mentioned cases. The reaction here considered proceeds according to the following equations: (1) $CMe_2Br\cdot CO_2Et + Zn = ZnBr\cdot CMe_2\cdot CO_2Et$; (2),

$$ZnBr\cdot CMe_2\cdot CO_2Et + CH_2<\substack{O\\O}>C_6H_3\cdot CHO =$$



$$CH_2<\substack{O\\O}>C_6H_3\cdot CH(OZnBr)\cdot CMe_2\cdot CO_2Et;$$

and (3), this last



$$+ H_2O = ZnBr\cdot OH + CH_2<\substack{O\\O}>C_6H_3\cdot CH(OH)\cdot CMe_2\cdot CO_2Et.$$

β-Hydroxy-β-piperonyl-α-dimethylpropionic acid,

$$CH_2{:}O_2{:}C_6H_3\cdot CH(OH)\cdot CMe_2\cdot CO_2H,$$

separates from water in slender crystals which melt and decompose at 156°; it is readily soluble in alcohol or ether and has the normal molecular weight in boiling ether. The *sodium* (with $4H_2O$), *barium* (with $6H_2O$), and *silver* salts were prepared and analysed. When heated with dilute sulphuric acid, the acid gives up carbon dioxide and water, forming 2 : 3-*methylenedioxy*-1-*isobutylenebenzene*,

$$CMe_2{:}CH{\cdot}C_6H_3{:}O_2{:}CH_2,$$

which boils at 252—254° and has the sp. gr. 1·094 at 22°/22°.

T. H. P.

Asymmetric Synthesis. By EMIL FISCHER and MAX SLIMMER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 597—610).—*Tetra-acetylhelicin*, obtained by the action of acetic anhydride on helicin in presence of sodium acetate, melts at 142° (corr.). In solution in benzene, it has $[\alpha]_D$ $-23{\cdot}48°$ at 20°; whilst in solution in acetone it has $[\alpha]_D$ $-37{\cdot}15°$ at 20°.

When treated with anhydrous hydrogen cyanide, it liquefies at first, then crystals of *tetra-acetylhelicin cyanohydrin*,

$$C_6H_7O_5Ac_4{\cdot}O{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN,$$

separate. This compound is easily soluble in chloroform, acetone, or hot alcohol, sparingly in ether or benzene, and almost insoluble in water; it melts at 162° (corr.) and has $[\alpha]_D$ $-24{\cdot}32°$ at 20°. The conversion of the cyanohydrin into *tetra-acetylgluco-o-hydroxymandelamide* can be effected by the action of hydrogen chloride, but special precautions are necessary; it melts at 205° (corr.). Saponification of the amide to gluco-*o*-hydroxymandelic acid was not possible, but when warmed with dilute mineral acids, it gave active o-*hydroxymandelic acid*,

$$HO{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CO_2H,$$

which has $[\alpha]_D$ $+1{\cdot}9°$ at 20°. Preparation of this active *o*-hydroxymandelic acid without isolation of the amide led to a product with $[\alpha]_D$ $+1{\cdot}3°$ at 20°.

This is pointed out as a case where, by synthesis, an active asymmetric compound is produced. On account of the small rotatory power of the product and the consequent indefiniteness of the proof of this important synthesis, another reaction has been tried to bring about the desired end, namely, by producing a carbinol through the intervention of zinc alkyl.

When tetra-acetylhelicin is treated in benzene solution with zinc ethyl and the resulting product decomposed with water, *tetra-acetylgluco-o-hydroxyphenylethylcarbinol*, $C_6H_7O_5Ac_4{\cdot}O{\cdot}CHEt{\cdot}OH$, is obtained which crystallises in square plates melting at 156·5° (corr.), and having $[\alpha]_D$ $-30{\cdot}10°$ at 20°. When saponified in the cold with baryta water, it gives *gluco-o-hydroxyphenylethylcarbinol*, but this was not obtained in a satisfactory form. Without isolating this glucoside, the tetra-acetylcarbinol can be converted into active o-*hydroxyphenylethylcarbinol*, $HO{\cdot}C_6H_4{\cdot}CHEt{\cdot}OH$, by treating the mixture after saponification with baryta with sulphuric acid and extracting with ether. By distilling under a pressure of 0·3 mm., a thick, colourless oil was obtained which in acetone solution has $[\alpha]_D$ $-9{\cdot}83°$ at 20°. An active substance has, therefore, undoubtedly been produced by synthesis.

For the sake of comparison, inactive *o*-hydroxyphenylethylcarbinol has been prepared and incidentally the following compounds:—*Methylsalicylic chloride* was obtained as a colourless liquid boiling at 145° under 17 mm. pressure, by the action of thionyl chloride on methylsalicylic acid. This acid chloride in ethereal solution, when treated with zinc ethyl and the product decomposed with water, gives o-*methoxyphenyl ethyl ketone*, $OMe \cdot C_6H_4 \cdot COEt$, as a slightly yellow, sweet-smelling liquid which boils at 137° (corr.) under 16·5 mm. pressure. This methoxy-compound when heated at 110° in a sealed tube with concentrated hydrochloric acid gives o-*hydroxyphenyl ethyl ketone*, $OH \cdot C_6H_4 \cdot COEt$, which boils at 115° (corr.) under 15 mm. pressure, and resembles phenol in odour. Its sodium salt is sparingly soluble in concentrated alkali solution and crystallises easily from alcohol.

By reducing an alkaline solution of the ketone with sodium amalgam and extraction with ether, i-o-*hydroxyphenylethylcarbinol* is obtained; this boils at about 125—130° under 0·25 mm. pressure, is only slightly soluble in hot water, and is little volatile with steam. It is very easily resinified by mineral acids, and reduces Fehling's solution when heated. In all these properties it closely resembles the active compound described above. J. McC.

Disulphones. XI. Influence of Intranucleal Substituents on the Reactivity of Aromatic Aldehydes and Ketones.

By Theodor Posner (*Ber.*, 1902, **35**, 2343—2354. Compare Abstr., 1899, i, 604; 1900, i, 5, 16; 1901, i, 14, 88, 474, 703; this vol., i, 82, 220, 296).—Benzophenone and acetophenone interact only with the more reactive mercaptans, but do not condense with amyl or phenyl mercaptan.

Dithiobenzyldiphenylmethane (*benzophenonebenzylmercaptal*),
$$CPh_2(S \cdot CH_2Ph)_2,$$
produced by condensing benzophenone and benzyl mercaptan with hydrogen chloride dissolved in glacial acetic acid, crystallises from water in white needles melting at 144°.

Dibenzylsulphodiphenylmethane (*benzophenonedibenzylsulphone*),
$$CPh_2(SO_2 \cdot CHPh)_2,$$
results from the oxidation of the preceding substance dissolved in carbon tetrachloride with cold saturated potassium permanganate solution; it separates from alcohol as a white, crystalline powder melting at 204—208°. Acetophenone and benzyl mercaptan condense to yield an unstable, oily mercaptal, which, on oxidation, gives rise to *aa-dibenzylsulpho-a-phenylethane* (*acetophenonedibenzylsulphone*),
$$CMePh(SO_2 \cdot CH_2Ph)_2,$$
a compound crystallising from alcohol in pale yellow leaflets melting at 131—133°. The presence of a nitro-group in the ortho-position with respect to the carbonyl radicle greatly diminishes the reactivity of the aromatic aldehydes, and quite prevents the condensation of the corresponding ketones with the thioalcohols. On the other hand, the introduction of nitro-groups into the meta- or para-position actually increases the capacity for reaction, and *m*-nitroacetophenone interacts with the less reactive mercaptans, whereas these substance do not condense with acetophenone itself.

The oily mercaptal obtained from *o*-nitrobenzaldehyde and ethyl mercaptan yields, on oxidation, *diethylsulpho*-o-*nitrophenylmethane* (o-*nitrobenzaldehydediethylsulphone*), $NO_2 \cdot C_6H_4 \cdot CH(SO_2Et)_2$, crystallising from alcohol in lustrous, colourless needles melting at 138°.

Dibenzylsulpho-o-*nitrophenylmethane* (o-*nitrobenzaldehydedibenzylsul-*

phone), $NO_2\cdot C_6H_4\cdot CH(SO_2CH_2Ph)_2$, obtained in a similar manner, crystallises in white leaflets melting at 188—190°.

Diphenylsulpho-o-nitrophenylmethane (o-*nitrobenzaldehydediphenylsulphone*), $NO_2\cdot C_6H_4\cdot CH(SO_2Ph)_2$, produced by oxidising the condensation product of *o*-nitrobenzaldehyde and thiophenol, crystallises in thin flakes melting at 158—160°.

*Diethylsulpho-*m*-nitrophenylmethane* (m-*nitrobenzaldehydediethylsulphone*), separates in white, flocculent crystals and melts at 164°.

*Dithiobenzyl-*m*-nitrophenylmethane* (m-*nitrobenzaldehydebenzylmercaptal*), $NO_2\cdot C_6H_4\cdot CH(S\cdot CH_2Ph)_2$, forms colourless, granular crystals and melts at 56°; the corresponding *disulphone*,

$$NO_2\cdot C_6H_4\cdot CH(SO_2\cdot CHPh)_2,$$

is a white, crystalline powder melting at 194°.

*Diamylsulpho-*m*-nitrophenylmethane* (m-*nitrobenzaldehydediamylsulphone*), $NO_2\cdot C_6H_4\cdot CH(SO_2\cdot C_5H_{11})_2$, crystallises from hot alcohol in white leaflets and melts at 120—122°; the corresponding *diphenyldisulphone*, $NO_2\cdot C_6H_4\cdot CH(SO_2Ph)_2$, melts at 176°.

*Dithiobenzyl-*p*-nitrophenylmethane* (p-*nitrobenzaldehydebenzylmercaptal*), $NO_2\cdot C_6H_4\cdot CH(S\cdot CH_2Ph)_2$, crystallises from alcohol in colourless needles or leaflets, melts at 72—74°, and yields a *disulphone* separating from glacial acetic acid as a yellow, crystalline powder melting at 244°.

p-Nitrobenzaldehyde also yields a *diethyldisulphone*,

$$NO_2\cdot C_6H_4\cdot CH(SO_2Et)_2,$$

a white, crystalline powder melting at 172°; a *diamyldisulphone*, $NO_2\cdot C_6H_4\cdot CH(SO_2\cdot C_5H_{11})_2$, crystallising in white leaflets and melting at 108—110°; a *diphenyldisulphone* forming colourless needles and melting at 210—212°.

*aa-Diethylsulpho-*m*-nitro-a-phenylethane* (m-*nitroacetophenonediethylsulphone*), $NO_2\cdot C_6H_4\cdot CMe(SO_2Et)_2$, derived from *m*-nitroacetophenone and ethyl mercaptan, forms lustrous, white needles melting at 140—142°.

*aa-Dithiobenzyl-*m*-nitro-a-phenylethane* (m-*nitroacetophenonebenzylmercaptal*), $NO_2\cdot C_6H_4\cdot CMe(S\cdot CH_2Ph)_2$, is obtained in granular crystals melting at 82—84°; the corresponding *disulphone* is a crystalline powder melting at 128—130°.

*aa-Diamylsulpho-*m*-nitro-a-phenylethane* (m-*nitroacetophenonediamylsulphone*), $NO_2\cdot C_6H_4\cdot CMe(SO_2\cdot C_5H_{11})_2$, and the corresponding *diphenyldisulphone*, crystallise from alcohol in needles melting respectively at 130—133° and 160—163°.

*aa-Diethylsulpho-a-*p*-nitro-a-phenylethane* (p-*nitroacetophenonediethylsulphone*), $NO_2\cdot C_6H_4\cdot CMe(SO_2Et)_2$, is readily obtained from *p*-nitroacetophenone and ethyl mercaptan; it separates from alcohol in pale yellow leaflets and melts at 108—110°.

m-*Nitrophenyldiethylsulphophenylmethane* (m-*nitrobenzophenonediethylsulphone*), $NO_2\cdot C_6H_4\cdot CPh(SO_2Et)_2$, derived from *m*-nitrobenzophenone and ethyl mercaptan, is a crystalline powder melting at 175°.

m-*Nitrophenyldibenzylsulphophenylmethane* (m-*nitrobenzophenonedibenzylsulphone*), $NO_2\cdot C_6H_4\cdot CPh(SO_2\cdot CH_2Ph)_2$, is a white powder, crystallising from alcohol and melting at 184—186°.

p-*Nitrophenyldiethylsulphophenylmethane* (p-*nitrobenzophenonediethylsulphone*), $NO_2\cdot C_6H_4\cdot CPh(SO_2Et)_2$, crystallises from alcohol as a pale yellow powder and melts at 193·5°.

p-*Nitrophenyldibenzylsulphophenylmethane* (p-*nitrobenzophenonedibenzylsulphone*), $NO_2\cdot C_6H_4\cdot CPh(SO_2\cdot CH_2Ph)_2$, crystallises in colourless needles and melts at 204°.

It was not found possible to condense the mercaptans with aromatic aldehydes or ketones containing hydroxy- or amidogen radicles. Crystalline products were obtained by the oxidation of the *m*- and *p*-amino-derivatives of benzophenone, but these compounds were found to be azo-derivatives containing no sulphur.

m-*Azobenzophenone*, $N_2(C_6H_4\cdot COPh)_2$, crystallises from alcohol in yellowish-brown leaflets and melts at 141—142°; *p*-azobenzophenone separates from ethyl acetate in red leaflets having a metallic reflex and melting at 217°.

The disulphones containing nitro-groups in the ortho- or para-position with respect to the carbonyl carbon atom are quite indifferent towards tin and hydrochloric acid and not altered by prolonged heating with this reagent.

The disulphones derived from *m*-nitroacetophenone and the diethyldisulphones are readily reduced to aminodisulphones, but the yields are small; the disulphones from *m*-nitrobenzaldehyde and *m*-nitrobenzophenone do not usually give rise to definite reduction products.

aa-Diethylsulpho-m-*amino-a-phenylethane* (m-*aminoacetophenonediethylsulphone*), $NH_2\cdot C_6H_4\cdot CMe(SO_2Et)_2$, is a pale yellow, crystalline substance melting at 136—138°; it crystallises from alcohol and is readily soluble in dilute hydrochloric acid.

aa-Dibenzylsulpho-m-*amino-a-phenylethane* (m-*aminoacetophenonedibenzylsulphone*), $NH_2\cdot C_6H_4\cdot CMe(SO_2\cdot CH_2Ph)_2$, and the corresponding *aminodiphenylsulphone*, $NH_2\cdot C_6H_4\cdot CMe(SO_2Ph)_2$, are yellow, crystalline powders readily soluble in alcohol or in mineral acids; they melt respectively at 180—182° and 158—160°.

m-*Aminophenyldiethylsulphophenylmethane* (m-*aminobenzophenonediethylsulphone*), $NH_2\cdot C_6H_4\cdot CPh(SO_2Et)_2$, is a white, crystalline powder melting at 183—184°; it dissolves in cold dilute hydrochloric acid, and the solution rapidly yields a sparingly soluble *hydrochloride*, which separates in aggregates of silky needles melting at 201°. G. T. M.

Compounds of Aromatic Ketones with Orthophosphoric Acid. By AUGUST KLAGES (*Ber.*, 1902, **35**, 2313—2315).—Diortho-substituted aromatic ketones do not form additive compounds with phosphoric acid (compare Klages and Allendorff, Abstr., 1898, i, 477); ketones of the type of acetophenone, however, give, as a rule, salts of the general formula $COPhR,H_3PO_4$. Thus acetophenone, *p*-diacetylbenzene, *p*-acetyltoluene, *p*-acetylethylbenzene, acetyl-*o*-xylene, acetyl-*p*-xylene, acetyl-*m*-xylene, diacetyl-*m*-xylene, acetyl-ψ-cumene, acetylcumene, acetylanisole, acetylphenetole, and acetylthienone give salts with phosphoric acid and acetophenone, *p*-acetyltoluene, *p*-acetylethylbenzene, acetyl-ψ-cumene, and acetylanisole salts with arsenic acid. *o*- and *m*-Acetyltoluenes and acetyl-*p*-cymene fail to give such derivatives.

Aliphatic aromatic ketones in which the alkyl radicle combined with the carbonyl group is greater than CH_3, do not, as a rule, form salts with phosphoric acid; this was found to hold in the case of propionylbenzene, *p*-propionyltoluene, butyryl- and *iso*butyryl-benzene, butyryl-*m*-xylene, *p*-propionylethylbenzene, propionylanisole, propionylphenetole, and butyrylphenetole. Propionyl ψ-cumene is an exception, as it gives a well-defined salt. W. A. D.

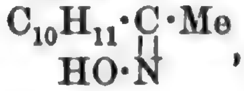
Action of Hydroxylamine on some Halogen Derivatives of Acetophenone. By A. Collet (*Bull. Soc. Chim.*, 1902, [iii], **27**, 539—543).—β-*p*-Dichloroacetophenoneoxime, $CH_2Cl·C(NOH)·C_6H_4Cl$, obtained by the action of hydroxylamine hydrochloride on the corresponding ketone in methyl alcoholic solution, forms slender, white needles which melt at 100·5—101° and are insoluble in water, sparingly soluble in cold, more so in hot light petroleum or carbon disulphide. When heated on the water-bath with concentrated sulphuric acid, it is converted into *chloroacetyl*-p-*chloroanilide*, $CH_2Cl·CO·NH·C_6H_4Cl$. β-*Bromo*-p-*chloroacetophenoneoxime*, obtained in a similar manner to the preceding oxime, separates from its solution in carbon disulphide in colourless, silky needles, soft to the touch, which melt at 106·5° and are soluble in hot light petroleum. When heated with concentrated sulphuric acid, it yields *bromoacetyl*-p-*chloroanilide*.

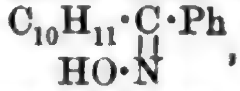
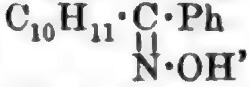
β-*Chloro*-p-*bromoacetophenoneoxime* forms very light, slender, colourless, silky needles which melt at 115°. Sulphuric acid converts it into *chloroacetyl*-p-*bromoanilide*, which melts at 180—181°. β-p-*Dibromoacetophenoneoxime* forms lustrous, colourless needles melting at 115°. The corresponding anilide melts at 169—170°. ββ-*Dibromo*-p-*chloroacetophenoneoxime* forms small, colourless crystals, which do not melt sharply, fusion taking place at 102—108°; it is very soluble in methyl or ethyl alcohol, and in benzene, less so in carbon disulphide. The corresponding *dibromoacetyl*-p-*chloroanilide* melts at 162—163°. ββ-p-*Tribromoacetophenoneoxime* forms colourless crystals melting at 111—112°, readily soluble in methyl or ethyl alcohol or in benzene, carbon disulphide, or light petroleum. *Dibromoacetyl*-p-*bromoanilide* melts slightly above 170°. p-*Chlorophenylglyoxime*,

$$C_6H_4Cl·C(NOH)·CH(NOH)\ [Cl:C=4:1],$$

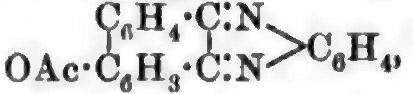
obtained by the action of hydroxylamine hydrochloride on dibromoethyl-*p*-chlorophenylketone, melts at 198—199°, and crystallises from alcohol in light, slender, colourless needles, insoluble in water, very soluble in methyl or ethyl alcohol, and in ether, sparingly so in benzene. p-*Bromophenylglyoxime* is a colourless, crystalline powder melting at 171—172°; it is insoluble in water, very soluble in methyl or ethyl alcohol, soluble in boiling benzene.

For purposes of identification, the author has also prepared a number of the anilides described above by the action of the chloride of chloroacetyl and of bromoacetyl on *p*-chloroaniline or *p*-bromoaniline, the reaction being moderated by dissolving the acid chloride in carbon disulphide. A. F.

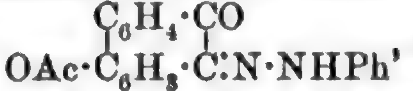
Ketones and Oximes containing a Tetrahydronaphthalene Nucleus. By W. Scharwin (*Ber.*, 1902, **35**, 2511—2515).—*Tetrahydronaphthyl methyl ketone*, obtained by the action of acetyl chloride on tetrahydronaphthalene in presence of aluminium chloride, is a colourless, aromatic liquid which boils at 152° under 12 mm. pressure. The only *oxime* obtained crystallises in colourless needles, melts at 106°, and has the configuration  $\begin{array}{r}C_{10}H_{11}\cdot C\cdot Me\\ \Vert\ \ \ \ \ \ \\ HO\cdot N\ \ \ \ \ \ \end{array}$, which is shown by its transformation into aceto-β-tetrahydronaphthalide.

Phenyl tetrahydronaphthyl ketone is a viscous, yellow liquid which boils at 222—223° under 12 mm. pressure. The crude oxime can be separated by fractional crystallisation from acetic acid and alcohol into the less soluble *oxime*,  $\begin{array}{r}C_{10}H_{11}\cdot C\cdot Ph\\ \Vert\ \ \ \ \ \ \\ HO\cdot N\ \ \ \ \ \ \end{array}$, which melts at 142°, and can be transformed into *benzoyl-β-tetrahydronaphthalide* (m. p. 166—167°), and its *stereoisomeride*,  $\begin{array}{l}C_{10}H_{11}\cdot C\cdot Ph\\ \ \ \ \ \ \ \ \ \ \ \Vert\\ \ \ \ \ \ \ \ \ \ \ N\cdot OH\end{array}$, which melts at 116°, and can be transformed into the *anilide* of tetrahydronaphthoic acid (m. p. 153°). R. H. P.

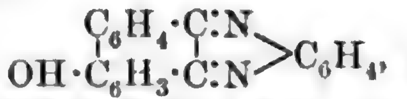
Phenanthrene. II. By Alfred Werner [and, in part, Tobias Frey, A. Grob, H. Heil, Johannes Kunz, Max Kunz, Bernh. Löwenstein, Adolf Ney, K. Rekner, Adolf Scherrer, H. Schwabacher, and Ad. Wack] (*Annalen*, 1902, **322**, 135—173. Compare this vol., i, 437).—3-*Acetoxyphenanthraquinone*, $C_{14}H_7O_2\cdot OAc$, produced by oxidising 3-phenanthryl acetate with chromic acid in glacial acetic acid solution, crystallises from this solvent in golden-yellow needles melting at 199—201°. 3-*Acetoxyphenanthraphenazine*,



$$\begin{array}{r}C_6H_4\cdot C\!:\!N\\ |\quad\ \ |\ \ \ \\ OAc\cdot C_6H_3\cdot C\!:\!N\end{array}\!\!>\!C_6H_4,$$

obtained by condensing the preceding compound dissolved in glacial acetic acid with *o*-phenylenediamine in alcoholic solution, crystallises from alcohol or benzene in yellow needles melting at 223—225°. The *phenylhydrazone*,  $\begin{array}{l}\ \ \ \ \ \ \ C_6H_4\cdot CO\\ \ \ \ \ \ \ \ |\quad\ \ \ \ |\\ OAc\cdot C_6H_3\cdot C\!:\!N\cdot NHPh\end{array}$, of this quinone is obtained in red needles with a green reflex; it is readily soluble in the ordinary organic solvents and melts at 207—209°.

3-*Hydroxyphenanthraquinone* may be prepared either by hydrolysing the preceding acetyl compound or by treating 3-aminophenanthraquinone with sodium nitrite in the presence of dilute sulphuric acid; it sublimes in brick-red needles and has no definite melting point. The hydrolysis is effected by dissolving the acetyl compound in concentrated sodium hydrogen sulphite solution saturated with ether; the latter solvent is necessary, otherwise the quinone does not pass into solution. The hydroxy-derivative is separated by distilling off the ether and acidifying the residual solution with a mineral acid; it is shown to be identical with the substance obtained from 3-aminophenanthraquinone by acetylating the latter hydroxyquinone with acetic anhydride; the product crystallises in the characteristic golden-yellow needles melting at 200—201°.

3-*Hydroxyphenanthraphenazine*,  $\begin{array}{r}C_6H_4\cdot C\!:\!N\\ |\quad\ \ |\ \ \ \\ OH\cdot C_6H_3\cdot C\!:\!N\end{array}\!\!>\!C_6H_4$, produced by hydrolysing the corresponding acetyl derivative with alcoholic potassium hydroxide solution, is insoluble in the ordinary organic solvents and separates from pyridine, on adding water, as a yellow, crystalline powder infusible below 340°. 3-*Hydroxyphenanthraquinone phenylhydrazone*, obtained in a similar manner from the phenylhydrazone of the acetoxyquinone, crystallises from glacial acetic acid in red needles and melts at 235—238°; it is readily soluble in the ordinary organic solvents.

3-*Benzoyloxyphenanthraquinone*, $C_{14}H_7O_2{\cdot}OBz$, obtained by oxidising 3-phenanthryl benzoate with chromic acid, crystallises from glacial acetic acid in lustrous, yellow needles and melts at 224—226°; the corresponding *phenazine* is an amorphous, yellow powder melting at 234—236°.

3-*Benzenesulphophenanthraquinone*, $C_{14}H_7O_2{\cdot}O{\cdot}SO_2Ph$, produced by the oxidation of 3-phenanthrylbenzenesulphonate, crystallises from glacial acetic acid in dark-yellow leaflets melting at 216—218°.

3-*Methoxyphenanthraquinone*, $C_{14}H_7O_2{\cdot}OMe$, results from the oxidation of 3-phenanthryl methyl ether with chromic acid; it crystallises from glacial acetic acid in orange-yellow needles and melts at 204—205°. The yield is small owing to the formation of a dimethoxydiketodiphenanthryl. This quinone is undoubtedly identical with Pschorr's 3-methoxyphenanthraquinone which melts at 206° (Abstr., 1900, i, 233).

3-*Ethoxyphenanthraquinone* crystallises from glacial acetic acid or alcohol in orange-coloured needles and melts at 207—208°; it may be obtained either by oxidising phenanthryl ethyl ether or by condensing *p*-ethoxyphenyl-*o*-aminocinnamic acid; the starting point in the latter synthesis being *p*-hydroxybenzyl cyanide.

p-*Ethoxybenzyl cyanide*, $OEt{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$, produced by alkylating the hydroxy-compound with ethyl iodide in alcoholic potassium hydroxide solution, crystallises from dilute alcohol in white leaflets melting at 47°.

p-*Ethoxyphenylacetic acid*, $OEt{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, is obtained either by hydrolysing the nitrile with alcoholic potassium hydroxide solution or by the direct action of ethyl sulphate on the hydroxy-nitrile in the presence of excess of the alkali hydroxide; the substance is liberated by mineral acids and crystallises from dilute alcohol or hot water in colourless leaflets melting at 89°; when prepared according to the second process, it is accompanied by a certain amount of its amide, $OEt{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, a compound crystallising from water in white leaflets melting at 184°.

a-p-*Ethoxyphenyl-*o*-nitrocinnamic acid*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}C(C_6H_4{\cdot}OEt){\cdot}CO_2H,$$

prepared by condensing *o*-nitrobenzaldehyde with the sodium salt of the preceding acid in the presence of excess of acetic anhydride at 130—150°, is extracted with sodium hydroxide solution, reprecipitated by mineral acids, and recrystallised from toluene or glacial acetic acid, forming amber-coloured, prismatic crystals melting at 158°. Although insoluble in water, it readily dissolves in the ordinary organic solvents excepting light petroleum.

a-p-*Ethoxyphenyl-*o*-aminocinnamic acid*,

$$NH_2{\cdot}C_6H_4{\cdot}CH{:}C(C_6H_4{\cdot}OEt){\cdot}CO_2H,$$

obtained by reducing the preceding compound with ferrous sulphate in ammoniacal solution, separates on adding dilute hydrochloric acid to the filtered solution in two modifications, one being white and the other yellow. The former variety is always accompanied by the latter and both forms melt at 189°. The acid is insoluble in water or dilute mineral acids, but readily dissolves in solutions of the alkali hydroxides or in the ordinary organic solvents. When treated with sodium nitrite in the presence of dilute sulphuric acid, a diazo-derivative is produced which on adding copper powder undergoes condensation to yield 3-*ethoxyphenanthrene*-10-*carboxylic acid*; this product crystallises from alcohol in greyish-white leaflets melting at 206°, and furnishes 3-ethoxyphenanthraquinone on oxidation with chromic acid.

3-Hydroxyphenanthraquinone, on treatment with excess of nitric acid at 50°, yields *mononitro*-3-*hydroxyphenanthraquinone*, a compound crystallising in yellow needles and melting at 259—260°; 3-methoxyphenanthraquinone also yields a nitro-compound which, however, was not obtained pure; these nitro-derivatives give rise to amines on reduction. 3-Acetoxyphenanthraquinone, when nitrated, furnishes two nitro-derivatives, a *mononitro*-compound crystallising in golden-yellow needles and melting at 217°, and a *dinitro*-compound melting at 263—265°. When the acetoxyquinone is treated with nitric acid at the boiling point, a third nitro-product is formed which crystallises in pale yellow needles and melts at 200—201°.

2-*Hydroxyphenanthraquinone*, obtained by oxidising 2-phenanthryl acetate with chromic acid, extracting the product with sodium hydrogen sulphite, and decomposing the additive compound with warm dilute sulphuric acid, crystallises from glacial acetic acid in slender, violet-black needles melting at 280—283°. This compound may also be produced in much better yield by the action of nitrous acid on 2-aminophenanthraquinone. 2-*Acetoxyphenanthraquinone*, $C_{14}H_7O_2\cdot OAc$, results from the action of acetic anhydride on the hydroxyquinone at 120—130°; it crystallises from light petroleum in needles or plates melting at 215—216°.

2-*Benzoyloxyphenanthraquinone*, prepared either by the oxidation of 2-phenanthryl benzoate or by subjecting the hydroxyquinone to the Schotten-Baumann reaction, crystallises from benzene in yellow needles melting at 240—242°.

2-*Benzenesulphophenanthraquinone*, $C_{14}H_7O_2\cdot O\cdot SO_2Ph$, produced by a modification of the latter reaction, is a light-brown, uncrystallisable powder.

2-*Phenanthryl methyl ether*, $C_{14}H_7O_2\cdot OMe$, readily obtained by methylating the hydroxy-compound with dimethyl sulphate in the presence of potassium hydroxide solution, crystallises from glacial acetic acid in dark red needles melting at 170—171°.

2-*Phenanthryl ethyl ether*, $C_{14}H_7O_2\cdot OEt$, produced in a similar manner by the action of ethyl sulphate, crystallises in red leaflets and melts at 160—161°; these ethers may also be prepared by the action of the corresponding alkyl iodides in the presence of the alcoholic sodium alkyloxides, but only a very small amount of the methyl ether is thus obtained.

2-Methoxyphenanthraquinone, when distilled with soda-lime, gives rise to 2-*methoxyfluorenone*, $C_{14}H_{10}O_2$, and 2-methoxyfluorene; the former crystallises in orange-yellow needles and melts at 106—108°; these products were identified by comparison with specimens directly prepared from 2-hydroxyfluorenone and 2-hydroxyfluorene respectively.

Bromophenanthraquinone, prepared by oxidising dibromophenanthrene, crystallises from glacial acid in nodular aggregates melting at 126°; the position of the bromine atom has not yet been determined.

In preparing 3-hydroxyphenanthraquinone from 3-benzoyloxyphenanthraquinone, a bye-product is obtained which does not dissolve in sodium hydrogen sulphite solution. This substance, *dibenzoyloxydiphenanthronylene*, $CO{:}C_{12}H_7(OBz){:}C{:}C{:}C_{12}H_7(OBz){:}CO$, crystallises from glacial acetic acid in reddish-yellow needles melting at 205—206°.

Dibenzoyldiacetyltetroxydiphenanthryl,

$$OAc{\cdot}CH{:}C_{12}H_7(OBz){:}C{:}C{:}C_{12}H_7(OBz){:}CH{\cdot}OAc,$$

obtained by reducing the preceding compound with zinc and hydrochloric acid and treating the unstable dihydric alcohol with acetic anhydride, crystallises from glacial acetic acid in lustrous, white needles melting at 225—226°. G. T. M.

Dibromoxyloquinhydrone. By G. Teichner (*Ber.*, 1902, **35**, 2303—2304).—The dark coloured substance melting at 169—170° obtained by Auwers and Sigel (this vol., i, 216) by the oxidation of halogen derivatives of ψ-phenols, which was thought by them to be dibromoxyloquinone, is in reality *dibromoxyloquinhydrone*. This compound can be prepared by the union of the quinone with the corresponding quinol, and is converted by oxidation into the quinone melting at 184°, by reduction into the quinol melting at 174—175°.

A. H.

Preparation of Anthrachrysone. By W. Hohenemser (*Ber.*, 1902, **35**, 2305—2306).—The disulphobenzoic acid requisite for this preparation is best obtained by heating benzoic acid with 4·5 parts of fuming sulphuric acid containing 70 per cent. of anhydride in sealed tubes for 3 hours at 250° (compare Barth and Senhofer, *Annalen*, 1871, **159**, 218). At 100°, the fuming sulphuric acid only produces monosulphobenzoic acid. The condensation to anthrachrysone is effected by heating the disulpho-acid at 100° for 1 hour with 10 parts of pure sulphuric acid. A. H.

Isomerism in the Benzylidenementhones, and the Preparation of an a-Methyl-δ-*iso*propyladipic Acid identical with Dihydrocamphoric Acid. By Camille Martine (*Compt. rend.*, 1902, **134**, 1437—1439).—From the oily products obtained in the preparation of benzylidene-menthone (Abstr., 1901, i, 599), two substances can be isolated, which appear to be two isomeric *benzylidenementhones*; the one, which is formed in much larger quantity, crystallises in plates melting at 51°, and has $[\alpha]_D$ $-185°50'$; its *oxime* crystallises in slender needles melting at 172°. The other forms long needles melting at 47°, and has $[\alpha]_D$ $-258·5°$; its *oxime* melts at 153°.

α-Methyl-δ-*iso*propyladipic acid, $CO_2H{\cdot}CHMe{\cdot}C_2H_4{\cdot}CHPr^{\beta},CO_2H$, is obtained, together with benzoic acid, when the benzylidenementhone

(m. p. 51°) is oxidised with dilute aqueous permanganate; it melts at 105° and is inactive to polarised light; when boiled with acetic anhydride, it gives an anhydride, $C_{10}H_{16}O_3$, which, on prolonged heating, loses carbon dioxide and is converted into a *ketone*, $C_9H_{16}O$, having the odour of menthone and boiling at 180—181°; the *semicarbazone* of the latter melts at 205°. The methyl*iso*propyladipic acid is shown to be identical with the dihydrocamphoric acid obtained by Crossley and Perkin (Trans., 1898, **73**, 23) by fusing camphoric acid with potassium hydroxide. The ketone just mentioned is probably α-methyl-δ-*iso*propylketo*cyclo*pentane. K. J. P. O.

Xanthamides of the Terpene Series. By L. Tschugaeff (*Ber.*, 1902, **35**, 2473—2483. Compare Abstr., 1900, i, 129, 352; 1901, i, 38).—Although the methyl xanthic esters of the alcohols, C_nH_{2n+1},OH, decompose at a low temperature into the corresponding olefine, carbon oxysulphide, and methyl mercaptan, this is not true of the esters of these alcohols with ordinary acids. Thus *menthyl oxalate*, which melts at 67—68° and has $[\alpha]_D$ −101·5° in benzene solution ($c = 1·902$), can be distilled without decomposition at 225° under a pressure of 12 mm., and can be heated to a much higher temperature without decomposing. The same is true of *menthyl carbonate*, *menthyl succinate*, *menthyl acetate*, which boils at 227°, *diphenylmenthylurethane*, &c. Menthyl benzoate is also very stable, but after being heated for 10 hours at 250° in a sealed tube, decomposes to a small extent, yielding menthene and benzoic acid.

It has been shown previously that the dixanthides are readily decomposed in the same way as xanthic esters, and this observation has now been extended to the xanthamides, which are obtained by the action of alcoholic ammonia on the corresponding xanthic methyl esters (Debus).

Menthylxanthamide, $C_{10}H_{19}O{\cdot}CS{\cdot}NH_2$, crystallises in small needles melting at 144—145°, is almost insoluble in water, and has the normal molecular weight. It has $[\alpha]_D$ −115·9° in toluene ($c = 4·9927$), but this varies both with the concentration and with the nature of the solvent. The crystals show triboluminescence. When it is heated, it commences to decompose at about 200° and yields menthene, carbon oxysulphide, and other products. This decomposition is typical for all the xanthamides examined.

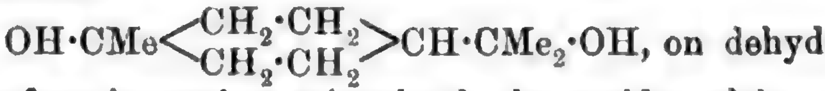
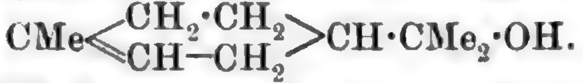
Bornylxanthamide, $C_{10}H_{17}O{\cdot}CS{\cdot}NH_2$, was prepared in both optical forms. These crystallise in long prisms, show triboluminescence, and melt at 125—126°. The *d*-amide has in benzene $[\alpha]_D$ +18·95° ($c = 6·4053$); the *l*-amide has $[\alpha]_D$ −18·13° ($c = 5·481$). These rotations are exceptional in being lower than those of the corresponding alcohols. *r-Bornylxanthamide* melts at 134·5—135·5°, and does not show triboluminescence.

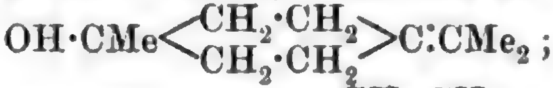
1-*Fenchylxanthamide*, $C_{10}H_{17}O{\cdot}CS{\cdot}NH_2$, crystallises in nacreous plates melting at 129—130°, and has $[\alpha]_D$ −78·51° ($c = 10·402$) in benzene. Methyl dihydrocarvylxanthate yields with ammonia a mixture of two amides, derived from two isomeric dihydrocarveols. The *α-amide* forms large crystals melting at 62·5—63·5°, and has $[\alpha]_D$ +135·33° ($c = 9·226$) in benzene. The dihydrocarveol obtained from it by hydrolysis boils at 222·5—223° and has

$[\alpha]_D$ +33·86°, sp. gr. 0·9204 at 20°/4°, and n_D 1·47818 at 20°. The *β-amide* could not be obtained pure, but the crude liquid gave on hydrolysis a dihydrocarveol boiling at 120° under 20 mm. pressure; $[\alpha]_D$ +7·64°, sp. gr. 0·9266 at 20°/4°, n 1·48087 at 20°. Thioamides and thiocarbamides give a deep blue coloration when they are heated with a few drops of benzophenone chloride, and can readily be recognised by this reaction. A. H.

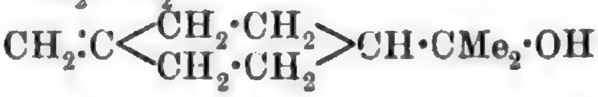
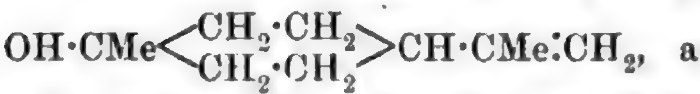
$\Delta^{8:9}$Terpen-1-ol: a New Terpineol Melting at 32°. By Karl Stephan and J. Helle (*Ber.*, 1902, **35**, 2147—2158).—Liquid terpineol, when distilled under diminished pressure, yields two principal fractions, the first boiling at 212—215° under the ordinary pressure, and having a sp. gr. 0·930 at 15°, and the second boiling at 218—220°, and having a sp. gr. 0·940 at 15°. Both these products solidify on cooling, the second fraction yielding after repeated crystallisation from alcohol, the well-known terpineol melting at 35—36°, whilst the first fraction furnishes a new isomeride melting at 32—33°.

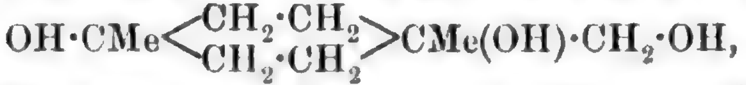
The terpineol melting at 35—36° boils at 98—99° under 10 mm., and at 218·8—219·4° under 752 mm. pressure; it has a sp. gr. 0·939 at 15°/15° and 0·935 at 20°/20°, n_D at 20° is 1·48132. Its *phenylurethane*, $C_{17}H_{23}O_2N$, melts at 112—113°; the *nitrosochloride* melts at 103°, and on treatment with piperidine readily yields the *nitrolepiperidide*, melting at 159°. On oxidation with dilute permanganate solution, trihydroxyhexahydrocymene is produced, and this, on further treatment with chromic acid, gives rise to the keto-lactone, $C_{10}H_{16}O_3$, melting at 62—63°. The new terpineol crystallises in needles, and boils at 90° under 10 mm., and at 209—210° under 752 mm. pressure; it has sp. gr. 0·923 at 15°/15°, and 0·919 at 20°/20°, n_D at 20° being 1·47470. The *phenylurethane* melts at 85°; the *nitrosochloride* melts at 102—103°, but does not readily yield a nitrolepiperidide. This terpineol is not readily acetylated, a fact which points to its being a tertiary alcohol.

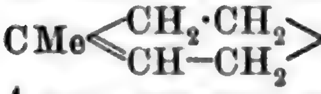
Terpin,  $OH\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$, on dehydration, may give rise to four isomeric terpineols, the isomeride melting at 35° being represented by the formula  $CMe<\begin{matrix}CH_2\cdot CH_2\\CH{-}CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$. To the compound melting at 60—70°, Baeyer ascribes the constitution



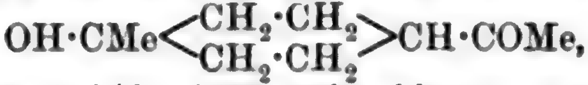
$$OH\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C{:}CMe_2\,;$$

the remaining formulæ,  $CH_2{:}C<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot OH$ and  $OH\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CMe{:}CH_2$, are available for the new substance, and the latter of these is considered to be the more probable, owing to the behaviour of the alcohol towards oxidising agents.

$\Delta^{8:9}$*Terpen-1-ol*, when treated with 1 per cent. potassium permanganate solution, yields the trihydric alcohol, 1 : 8 : 9-*trihydroxyhexahydrocymene*,  $OH\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CMe(OH)\cdot CH_2\cdot OH$, which crystallises from ethyl acetate or benzene in prisms melting at

118—118·5°; this product is soluble in warm water, the solution having a bitter taste. The trihydric alcohol, on oxidation with chromic acid, furnishes a ketone, p-*methyltetrahydroacetophenone*,  $\mathrm{CMe}{<}\begin{smallmatrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH{-}CH_2}\end{smallmatrix}{>}\mathrm{CH\cdot COMe}$, this product boiling at 68·5—70° under 4 mm. pressure, and having sp. gr. 0·9435 and n_D 1·47421 at 15°. The observed molecular refraction points to its containing one ethylene linking. The *semicarbazone*, $C_{10}H_7ON_3$, of the ketone crystallises in white leaflets and melts at 160°.

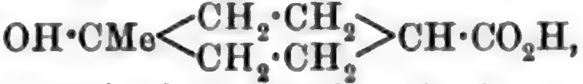
The oxidation of the trihydric alcohol also leads to the production of another ketone, p-*hydroxy*-p-*methylhexahydroacetophenone*,



$$\mathrm{OH\cdot CMe}{<}\begin{smallmatrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix}{>}\mathrm{CH\cdot COMe},$$

a compound boiling at 140—145° under 19 mm. pressure, and having a sp. gr. 1·023 and n_D 1·47548 at 20°; the corresponding *semicarbazone*, $C_{10}H_{19}O_2N_3$, melts at 195—196°.

An acidic substance, p-*hydroxyhexahydrotoluic acid*,



$$\mathrm{OH\cdot CMe}{<}\begin{smallmatrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix}{>}\mathrm{CH\cdot CO_2H},$$

melting at 153°, is obtained by treating the hydroxy-ketone with an alkaline solution of sodium hypobromite, bromoform being simultaneously produced. This acid is also formed by treating the trihydric alcohol with bromine and sodium hydroxide, only in this case the other product is tetrabromomethane. The acid contains hydroxyl, and yields with phenylcarbimide a phenylurethane melting at 162—163°; it forms a lactone, $C_8H_{12}O_2$, when distilled under the ordinary pressure; this product crystallises in serrated leaflets and melts at 68—69°. When, however, the hydroxy-acid is heated with 20 per cent. sulphuric acid, it loses the elements of water and becomes converted into tetrahydro-*p*-toluic acid (m. p. 98°), this substance being also produced by the action of sodium hypobromite on the unsaturated ketone. Warm concentrated sulphuric acid brings about an elimination of both water and hydrogen from the hydroxy-acid, giving rise to *p*-toluic acid. G. T. M.

Crystallographic Properties of Benzylidene-, Methylsalicylidene-, Ethylsalicylidene-, and Anisylidene-camphor, and of their Reduction Products. By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], 27, 544—549).—Dextro- and lævo-benzylidenecamphor crystallise in the forms of the rhombic system; the racemic compound, however, in the monoclinic system. In the case of anisylidenecamphor, the active as well as the racemic forms crystallise in rhombic prisms. *d*-Methylsalicylidenecamphor, and *d*-ethylsalicylidenecamphor both belong to the monoclinic system, the former crystallising in prisms, the latter in plates. Benzyl-, anisyl-, and ethyl-saligenylcamphor all crystallise in the rhombic system. A. F.

Some Reactions of Fenchone. By E. TARDY (*Bull. Soc. Chim.*, 1902, [iii], 27, 603—606).—If molecular proportions of a phenol and fenchone, previously heated to 60°, are mixed, the temperature rises and the resulting liquid has a higher rotatory power than fenchone;

the compound formed dissociates under the influence of solvents. α-Naphtholfenchone, obtained by mixing the two components at the ordinary temperature, forms white, flat, acicular crystals melting at 51°; β-naphtholfenchone forms large prisms melting at 57°. Both compounds readily dissociate, and when exposed to the air the fenone passes off, leaving the naphthols behind. Thymol, guaiacol, eugenol, and resorcinol also appear to form compounds with fenchone, the latter phenol combining with one or with two molecules of fenchone. They are all non-crystallisable.

Chloral also dissolves in fenchone and a crystalline compound can be obtained melting between 25° and 30°.

Fenchone also dissolves nitrocellulose, yielding a gelatinous mass which dissolves in ether; even a 10 per cent. solution of fenchone in alcohol dissolves nitrocellulose, forming a sort of collodion. A. F.

Some Further Constituents of the Essential Oil of Kaempferia Galanga. By Pieter van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, **4**, 618—620. Compare Abstr., 1900, i, 677).—Besides ethyl *p*-methoxycinnamate, previously found in the essential oil of *Kaempferia Galanga*, ethyl cinnamate has also been detected. Its isolation is difficult on account of the presence of an indifferent substance which congeals at about 10°. The fraction of the oil boiling at 155—165° under 30 mm. pressure was treated with 80 per cent. alcohol, which dissolved out the ethyl cinnamate. The insoluble residue, on repeated treatment with alcoholic potassium hydroxide, gave a liquid which was only slightly optically active and which became tinged with green on treatment with bromine. On purification by means of bromine, an inactive, colourless, odourless hydrocarbon of the formula $C_{15}H_{32}$ boiling at 267·5° under 738 mm. pressure was obtained which solidifies in a freezing mixture and melts at 10°. It has a sp. gr. 0·766 at 26° and its properties agree closely with those of *n*-pentadecane described by Krafft (Abstr., 1882, 1272).

J. McC.

Solubility of certain Fresh Resins. By Ch. Coffignier (*Bull. Soc. Chim.*, 1902, [iii], **27**, 549—555).—The solubility of a number of resins has been determined both by enclosing the resin in a cartridge of filter paper and extracting with a Soxhlet apparatus, and by boiling a weighed quantity of resin with a known volume of solvent. The chief results are as follows:—Dammar: completely soluble in oil of turpentine, but a small portion separates out when kept for some months; in ethyl alcohol at 95°, 28·6 per cent. insoluble; in amyl alcohol, 13 per cent. insoluble; completely soluble in chloroform, in hot benzene (the solution becomes slightly turbid on cooling), or in carbon tetrachloride; in ether, about 3·5 per cent. remains undissolved, and in amyl acetate about 2·73 per cent.; completely soluble in boiling amyl acetate. Sandarac: 73—82 per cent. insoluble in oil of turpentine; completely soluble in oil of spike, oil of rosemary, oil of cajeput, ethyl alcohol, or in amyl alcohol; 55 per cent. insoluble in chloroform, 67—85 per cent. insoluble in benzene; completely soluble in ether, in acetone, or in amyl acetate; 78 per cent. insoluble in carbon tetrachloride. Mastic: completely soluble in oil of turpentine; 36—37 per cent. insoluble in ethyl alcohol; completely soluble in amyl alcohol, benzene, chloroform, ether, carbon tetrachloride (hot), or amyl acetate (hot); 9·5 per cent. insoluble in acetone. A. F.

White Peru Balsam. By A. Biltz (*Chem. Zeit.*, 1902, **26**, 436). —On pouring white peru balsam into absolute alcohol, a white, brittle substance is obtained which melts at 120—130° and is soluble in benzene, ethyl acetate, or chloroform, insoluble in alcohol, ether, water, or alkalis. After removal of the alcohol, solution of the balsam in ether, and treatment with sodium carbonate solution to remove cinnamic acid, there separates a wax-like mass which crystallises from dilute alcohol in needles and melts at 260°. On treatment of the ethereal solution with 1 per cent. aqueous potassium hydroxide and acidification of the alkaline extract, there is formed a brownish-yellow precipitate which melts at about 100°. The remainder of the balsam is hydrolysed by alcoholic potassium hydroxide and distilled with steam. The oil so obtained is separated by fractional distillation under reduced pressure into cinnamyl alcohol and a colourless oil, probably of the formula $C_{20}H_{30}O$ or $C_{20}H_{28}O$, which has a pleasant odour, boils at 112° under 10 mm. pressure, has a sp. gr. 0·9433 at 17·5°, and on gentle oxidation yields benzaldehyde. The residue from the steam distillation is principally cinnamic acid. G. Y.

New Glucoside, Aucubin, contained in the Seeds of Aucuba Japonica. By Émile Bourquelot and Henri Hérissey (*Compt. rend.*, 1902, **134**, 1441—1443).—In order to extract the glucoside, *aucubin*, from the seeds of *Aucuba japonica*, the latter in a fresh state, are extracted with boiling 90 per cent. alcohol, into which passes the glucoside together with a relatively large quantity of sucrose. After completely distilling off the alcohol, the residue is diluted with water, and yeast is added to destroy the sugar. The glucoside is isolated by evaporating to dryness and crystallising the residue from alcohol; it forms tufts of elongated crystals melting at 181°, and has $[\alpha]_D$ $-173·1°$. Aucubin does not contain nitrogen or reduce Fehling's solution; it is hydrolysed by emulsin or by dilute sulphuric acid, forming dextrose, a substance with a penetrating odour and a brown principle insoluble in water.

K. J. P. O.

Researches on the Arrow Poisons from German East Africa. By Ludwig Brieger and G. Diesselhorst (*Ber.*, 1902, **35**, 2357—2359). —The arrow poison used by the Wapogorros, a tribe inhabiting the Ulunga plain in the south-west of German East Africa, contains an active principle which is first extracted with water, and then, after successive treatment with lead acetate and hydrogen sulphide, is removed by absolute alcohol from the residue left on evaporation. The solvent is again distilled off and the residue dissolved in water. A crystalline glucoside separates, which melts at 185—187° and contains $C = 56·01$; $H = 7·59$ per cent.; it is extremely poisonous, the lethal dose for a rabbit being 0·0005 gram per kilogram; the action of the drug resembles that of *Digitalis*. The mother liquor still possesses toxic properties, and yields another crop of crystals; these melt at 175—181°, and differ somewhat in composition for the first substance ($C=57{\cdot}11$; $H=7{\cdot}89$). In all probability, this poison contains a mixture of two poisonous glucosides, one of which is found in the poison employed by the Wakambas. The final mother liquors from the crystalline glucosides contain an amorphous glucoside, which, however, is non-poisonous. The communication contains a tabulated comparison of the arrow poisons employed by the tribes of German East Africa. G. T. M.

Theory of Dyeing. By Robert Gnehm and Felix Kaufler (*Zeit. angew. Chem.*, 1902, **15**, 345—348).—The barium salt of chrysophenin was obtained by boiling the free acid with barium chloride as a brown, amorphous powder; in boiling water, it is soluble to the extent of 0·095 per cent. The barium salt of benzopurpurin is soluble to the extent of 0·045 per cent. Cotton wool becomes coloured when immersed in solutions of these salts, and it has been proved that the salt (not the free acid) is absorbed. Absorption of salt has also been proved in the case of the corresponding sodium salts. Benzopurpurin can also be absorbed by cotton directly, although it is only soluble to the extent of about 0·001 per cent. Wool dyed with either the salt or the free acid may be extracted with water or salt solutions until there remains only a very small quantity of dye on the fibre. It is concluded that the dyeing is complete when equilibrium has been established between the inner and outer spaces of the cells. The results obtained are in good agreement with the theory proposed by Weber (*Färberzeit.*, 1894, 202), but the authors insist that the conclusions can only be applied to the class of dyes investigated and may not be extended to the explanation of all dyeing processes.

Lanuginic acid (Knecht and Appleyard, Abstr., 1889, 869) is not homogeneous, as has been proved by dialysis; it contains an appreciable quantity of a colloidal substance. J. McC.

Theory of the Dyeing Process. By Georg von Georgievics (*Chem. Zeit.*, 1902, **26**, 129—131).—An account, historical and critical, of the various papers published since 1894 on the theory of dyeing, which cannot be briefly abstracted. K. J. P. O.

Theory of the Dyeing Process. By P. D. Zacharias (*Chem. Zeit.*, 1902, **26**, 289—291).—The author draws attention to the fact that von Georgievics (preceding abstract) has misrepresented the theory of dyeing put forward by him (*Färber-Zeitung*, 1901, No. 10, 11).
K. J. P. O.

Theory of Dyeing. By Georg von Georgievics (*Chem. Zeit.*, 1902, **26**, 371).—A reply to Zacharias' criticism of the author's previous paper (compare preceding abstracts). K. J. P. O.

Criticism of the Dyeing-Theory of P. D. Zacharias. By Rudolf Wegscheider (*Chem. Zeit.*, 1902, **26**, 372). — Zacharias' mathematical treatment of the theory of dyeing is shown to be erroneous (compare preceding abstract). K. J. P. O.

Wool Mordants. By G. EBERLE and FR. ULFFERS (*Chem. Zeit.*, 1902, **26**, 406—407).—In answer to the criticism of von Georgievics (compare preceding abstracts), the authors have given a summary of their experimental investigation of the part played by the alkali salts usually added to the mordanting bath in the process of dyeing. It is found that these salts remove free acid which affects injuriously the development of a good colour. Thus only the alkali salts of weak acids are efficacious; the stronger the acid in the alkali salt, the less intense is the colour. K. J. P. O.

Adjective Colouring Matters of the Benzaldehyde Green and Rosamine Groups. By CARL LIEBERMANN (*Ber.*, 1902, **35**, 2301—2303).—The substitution of protocatechuic aldehyde for benzaldehyde in the preparation of colouring matters from dimethylaniline and *m*-dimethylaminophenol leads to the production of substances which readily dye with mordants. The substance produced from dimethylaniline is violet blue and dyes cotton violet to blue with alumina, blackish violet with iron, mordants. The derivative of *m*-dimethylaminophenol is coloured red and dyes a violet red on alumina and a gray violet on iron. The change of colour from green to blue by the introduction of two hydroxyl groups into the compound has been observed previously. A. H.

[Brazilin and Brazilein.] By CARL SCHALL (*Ber.*, 1902, **35**, 2306).—Brazilin becomes less soluble in acetic acid when it is preserved for a considerable time, and therefore a 10—16 per cent. solution in acetic acid should be used for the preparation of brazilein instead of a 30 per cent. solution. With brazilein, hydroxylamine in presence of hydrochloric acid yields a dioxime, in spite of the fact that hydroxylamine alone, as found by Herzig, reduces brazilein. A. H.

Comparison of Phylloporphyrin and Mesoporphyrin. By LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 223—226).—Contrary to Nencki and Zaleski's statement (Abstr., 1901, i, 434), the absorption spectrum of mesoporphyrin is found closely to resemble that of phylloporphyrin and not that of hæmatoporphyrin. After being treated with bromine, mesoporphyrin shows the absorption band in the extreme visible red, which is characteristic of phylloporphyrin but not of hæmatoporphyrin after similar treatment (compare Trans., 1900, **77**, 1091). Salts of hæmatoporphyrin dissociate electrolytically in aqueous solution; as a weaker base than phylloporphyrin, it requires a larger excess of free acid to prevent hydrolysis. G. Y.

Absorption of Ultra Violet Rays by Bilirubin, Biliverdin, Urobilin, and Proteinchrome. By L. BIER and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 230—232).—Contrary to what might be expected from the results obtained by Hartley (Trans., 1888, **53**, 641), the absorption spectra of bilirubin, biliverdin, urobilin, and proteinchrome show no characteristic bands in the ultra violet. The difference in behaviour of urobilin and of phylloporphyrin and hæmatoporphyrin is explained by the supposition that the absorption of violet rays depends, not on the constitution of the nucleus forming the basis of complicated substances, but rather on the presence of certain atomic groupings, which may not be present in all derivatives of the same parent-substance.

Urobilin must differ constitutionally more from the chromogen of the blood colouring matter than the latter does from chlorophyll.

G. Y.

Catechin. By M. KARNOWSKI and JOSEF TAMBOR (*Ber.*, 1902, **35**, 2408—2409).—The formulæ, $C_{25}H_{24}O_{11}$ and $C_{21}H_{21}O_7$, assigned to pentaacetylcatechin and acetylcatechin tetramethyl ether by Kostanecki and Tambor have been confirmed by determining the number of hydroxyl groups, and by molecular weight determinations from the boiling point of solutions in benzene. The mol. weight and the number of methoxyl groups of trimethylcatechone have also been found to be in agreement with the formula $C_{18}H_{18}O_7$.

Nitrotrimethylcatechone, $C_{18}H_{17}O_9N$, crystallises from alcohol in long, yellow needles, and melts at 141°, with liberation of gas.

T. M. L.

Catechin. By STANISLAUS VON KOSTANECKI and R. G. KREMBS (*Ber.*, 1902, **35**, 2410—2411).—The mol. weight and number of methoxyl groups of catechin tetramethyl ether are in agreement with the formula $C_{19}H_{22}O_6$. The *monobromo*-derivative, $C_{19}H_{21}BrO_6$, crystallises from alcohol in needles which decompose with frothing at 170°; its *acetyl* derivative, $C_{21}H_{23}BrO_7$, crystallises from much alcohol in silky, white needles, and melts (without frothing) at 172°. T. M. L.

Pyromucic Acid and *iso*Pyromucic Acid. Action of Phosphorus Pentachloride and Phosphorus Oxychloride. By G. CHAVANNE (*Compt. rend.*, 1902, **134**, 1439—1441. Compare Abstr., 1901, i, 649).—Pyromucic chloride, originally prepared by Liès-Bodart (*Annalen*, 1857, **100**, 327) by the action of phosphorus pentachloride on pyromucic acid, crystallises in prisms melting at −2°, and boiling at 170°; with ammonia, aniline, &c., it forms the amide, anilide, &c.

When phosphorus pentachloride is added to a solution of *iso*pyromucic acid in chloroform, or phosphoryl chloride is added to a suspension of sodium *iso*pyromucate in the same solvent, a substance is obtained which appears to be *iso*pyromucyl phosphate, $PO(O{\cdot}C_5H_3O_2)_3$; it crystallises in prisms melting at 138°. When left in contact, or warmed, with water, or dissolved in moist solvents, it is converted into a di*iso*pyromucyl phosphate, $OH{\cdot}PO(O{\cdot}C_5H_3O_2)_2$, which forms a crystalline powder containing $1H_2O$ and melting at 110—112°; when anhydrous it melts at 154°. It behaves as a monobasic acid, and its neutral solution gives white precipitates with silver, lead, and bismuth salts. By warming with normal sulphuric acid, it is hydrolysed to the mono-ester, $PO(OH)_2{\cdot}O{\cdot}C_5H_3O_2$.

Attention is drawn to the fact that *iso*pyromucic acid differs from its isomeride by giving a green colour with ferric chloride; and it is suggested that the *iso*-acid possesses phenolic or enolic characters.

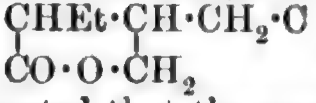
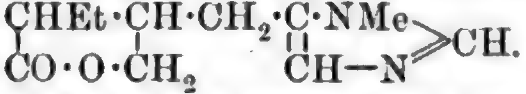
K. J. P. O.

Products of the Decomposition of *d*-Lupanine from Lupinus Albus. By ARTURO SOLDAINI (*Arch. Pharm.*, 1902, **240**, 260—272. Compare Abstr., 1893, i, 739; 1896, i, 193; and Davis, Abstr., 1897, i, 174).—A further investigation has been made of the products obtained when *d*-lupanine, $C_{15}H_{24}ON_2$, is brominated in acetic acid solution and the resulting tetrabromo-additive compound boiled with alcohol. In addition to the bases, $C_8H_{15}ON$ and $C_7H_{11}ON$ (originally described as $C_8H_{13}ON$ and C_7H_9ON), a third *base* was isolated; its platinichloride has a golden lustre and apparently decomposes at 211—212° without melting. C. F. B.

Oxidation of Morphine by the Extract of Russula Delica. By J. BOUGAULT (*Compt. rend.*, 1902, **134**, 1361—1363).—Oxymorphine hydrochloride is precipitated in a crystalline form from an aqueous solution of morphine hydrochloride treated with an excess of the extract of *Russula delica*, this decoction being produced by triturating the fresh fungus with a mixture of sand and dilute glycerol. The base oxymorphine isolated from its hydrochloride by sodium hydrogen carbonate is identical with the compound, known as ψ-morphine, dehydromorphine, or oxydimorphine, obtained by oxidising morphine with an alkaline solution of potassium ferricyanide (compare Polstorff, Abstr., 1880, 408). The base is very insoluble in chloroform, amyl alcohol, or ethyl acetate, these solvents taking up less than 0·005 per cent. of the substance; it is most conveniently dissolved in ammoniacal amyl alcohol. The optical rotation of the base is extremely variable in alkaline solution; the addition of sodium hydroxide causes the angle of rotation to diminish until a minimum is reached, beyond this point an increase of alkalinity augments the optical activity.

The salts of oxymorphine with the mineral acids are very sparingly soluble in water, and the base may be conveniently separated from morphine by means of the sulphates. The salts of oxymorphine with the organic acids are more soluble in water in presence of excess of the acid, but they do not dissolve in alcohol. Oxymorphine, dissolved in concentrated sulphuric acid and treated with a drop of dilute formaldehyde solution, develops a green coloration; under these conditions, morphine gives rise to a deep reddish-violet coloration. G. T. M.

Pilocarpine. Constitution of the Alkaloid. II. By ADOLF PINNER and RUDOLF SCHWARZ (*Ber.*, 1902, **35**, 2441—2459. Compare this vol., i, 232; and Jowett, Trans., 1900, **77**, 851; 1901, **79**, 580, 1331).—It has been shown by Jowett (*loc. cit.*) that with silver oxide *iso*pilocarpine methiodide yields a hydroxide which does not give precipitates with platinic chloride or picric acid until it has been boiled with hydrochloric acid. The authors point out that in the treatment with silver oxide the lactone ring, known to be present in pilocarpine and *iso*pilocarpine-methiodide, has been opened, and that the compound obtained by Jowett was *iso*pilocarpic acid methohydroxide, $C_{11}H_{18}O_3N_2,CH_3{\cdot}OH$, and not *iso*pilocarpine methohydroxide; and, further, on boiling this substance with acids, the lactone ring is again formed, *iso*pilocarpine methochloride being produced, and now giving a platinichloride.

Since, by oxidation of pilocarpine or *iso*pilocarpine with permanganate, homopilopic acid (of known constitution) is obtained (Jowett), the complex,  $\begin{array}{l}\mathrm{CHEt{\cdot}CH{\cdot}CH_2{\cdot}C}\\ \mathrm{CO{\cdot}O{\cdot}CH_2}\end{array}$, must be present in the alkaloids; further, it is suggested that the group $C_2H_2N{\cdot}NMe$ which, in the oxidation, is converted into ammonia, methylamine, and carbon dioxide, forms part of a glyoxaline ring, and therefore that pilocarpine (or *iso*pilocarpine) has the constitution  $\begin{array}{l}\mathrm{CHEt{\cdot}CH{\cdot}CH_2{\cdot}C{\cdot}NMe}\\ \mathrm{CO{\cdot}O{\cdot}CH_2\quad\; CH{-}N}\end{array}\!\!>\mathrm{CH}$.

Pilocarpine is found to behave as a glyoxaline derivative. It is shown that although methylglyoxaline is stable towards alkalis, methylglyoxaline-alkylhaloids are readily decomposed, yielding methylamine, the alkylamine, formic acid, and methyl alcohol. Pilocarpine and *iso*pilocarpine behave in an exactly similar manner; they are stable towards alkalis, but their alkyl salts decompose easily, yielding, besides formic and homopilopic acids, methylamine and the alkylamine. Pilocarpine forms a substituted product with bromine, as do the glyoxalines, and not an additive product. Pilocarpine and the glyoxalines are readily oxidised by permanganate and hydrogen peroxide, but not by chromic acid. Again, benzoyl chloride reacts with glyoxaline, but not with methylglyoxaline, and pilocarpine also is not attacked by benzoyl chloride.

Pilocarpine and *iso*pilocarpine cannot be stereoisomeric, as, when oxidised with chromic acid, the former yields pilocarpoeic acid, $C_{11}H_{16}O_5N_2$, whilst the latter is slowly broken up; also with bromine water quite different products are obtained.

Pilocarpine ethosulphate (from pilocarpine ethiodide and silver sulphate), pilocarpine propobromide and amylobromide were prepared, and their behaviour on boiling with 30 percent. potassium hydroxide studied, with the results previously described. The analogous decomposition of methylglyoxaline amylobromide, amylglyoxaline methiodide, and benzylglyoxaline methiodide was investigated.

When dibromopilocarpine or dibromo*iso*pilocarpine is boiled with barium hydroxide, barium dibromo*iso*pilocarpate is formed, from which the *acid* $C_{11}H_{16}O_3N_2Br_2$ can be prepared; the latter crystallises in needles melting at 120° and losing water at 122°, with the formation of dibromo*iso*pilocarpine (the lactone).

In the oxidation of pilocarpine by chromic acid, besides pilocarpoeic acid, a *substance*, $C_8H_{10}O_2N_2$, is formed, which crystallises in small plates melting at 153°; it probably does not contain the group which forms the lactone ring in pilocarpine.

Pilopic acid, $C_7H_{10}O_4$, obtained by Jowett in oxidising *iso*pilocarpine with permanganate, does not appear to be the lactone of pilomalic acid, $C_7H_{12}O_5$, prepared by oxidising pilocarpoeic acid, as on heating pilomalic acid a dibasic acid is obtained, whilst pilopic acid is monobasic; again, ethyl pilomalate yields an amide melting at 190—191°, whereas Jowett's diamide melts at 160°. K. J. P. O.

Conversion of Tropidine into Tropine. By ALBERT LADENBURG (*Ber.*, 1902, **35**, 2295—2297).—Polemical, in reply to Willstätter (this vol., i, 559). A. H.

Formation of 2-Pyrrolidinecarboxylic Acid by Alkaline Hydrolysis of Casein. By Emil Fischer (*Zeit. physiol. Chem.*, 1902, **35**, 227—229).—Casein is less readily hydrolysed by sodium hydroxide solution than by hydrochloric acid, but furnishes with the former a mixture of amino-acids from which, by the process already described (Abstr., 1901, i, 192), about 2·5 per cent. of crude 2-pyrrolidinecarboxylic acid in the lævo- and racemic forms was isolated (Abstr., 1901, i, 780). T. A. H.

Condensation Products of Pyrrole. By Giuseppe Plancher (*Ber.*, 1902, **35**, 2606—2608).—The base, $C_{12}H_{17}N$, formed from 2 : 5-dimethylpyrrole by reduction with zinc dust and glacial acetic acid, yields a *hydriodide*, $C_{12}H_{18}NI$, which crystallises in colourless prisms melting above 270°. Probably the 2 : 5-dimethylpyrrole is first hydrolysed to acetonylacetone, which, condensing with some of the unaltered compound, forms the base $C_{12}H_{15}N$, which finally undergoes reduction to $C_{12}H_{17}N$.

An intermediate *compound*, $C_{12}H_{15}N$, is obtained when 2 : 4-dimethylpyrrole is condensed with 90 per cent. acetic acid and zinc dust or zinc acetate; it crystallises in colourless needles and melts at 74°; the *aurichloride* forms light yellow needles or prisms melting at 109° and the *platinichloride* orange-red prisms decomposing at 213°. It does not combine with methyl iodide in the cold, and although giving a faint pine wood coloration and the indole reaction with anhydrous oxalic acid, does not furnish the ordinary pyrrole indications with isatin and phenanthraquinone.

The views put forward as to the preceding condensations are confirmed by condensing pyrrole with acetonylacetone, zinc acetate, and glacial acetic acid, when the *base* $C_{10}H_{11}N$ is produced; this crystallises in colourless needles, melts at 101—102°, gives the usual pyrrole colorations with isatin and pine wood, and develops a coloration with oxalic acid; it also yields a crystalline picrate. G. T. M.

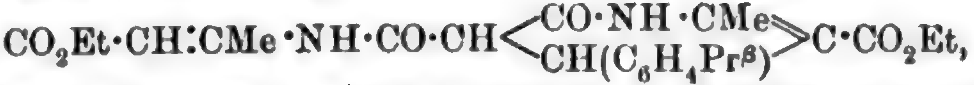
Action of Malonic Ether and Malonamide on Aminoacetylacetone. By Emil Knoevenagel and W. Cremer (*Ber.*, 1902, **35**, 2390—2396).—*Ethyl 2-hydroxy-4 : 6-lutidine-3-carboxylate*,

$$\mathrm{CMe}\Big\langle{}^{\mathrm{N{:}C(OH)}}_{\mathrm{CH{-}CMe}}\Big\rangle\mathrm{C{\cdot}CO_2Et},$$

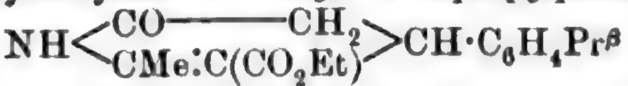
prepared by condensing ethyl malonate with aminoacetylacetone in presence of sodium, crystallises from alcohol in long, slender needles, and from water in glistening tablets, melts at 136°, and does not react with nitrous acid or with hydroxylamine. The *hydrochloride* melts at 95°. The free *acid*, $C_8H_9O_3N$, formed as a bye-product, crystallises from alcohol, melts at 254°, and yields ψ-lutidostyril when heated at 260°. The *amide*, prepared by condensing malonamide with aminoacetylacetone, crystallises from hot water with $1H_2O$, which it loses at 110°, melts at 224°, dissolves in hydrochloric acid and in aqueous sodium hydroxide, is hydrolysed when heated with strong potassium hydroxide, and yields ψ-lutidostyril when boiled with 25 per cent. hydrochloric acid. T. M. L.

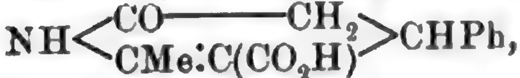
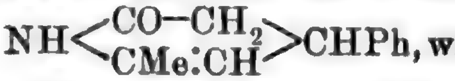
Syntheses in the Pyridine Series. IV. An Extension of Hantzsch's Dihydropyridine Syntheses. By Emil Knoevenagel and Richard Brunswig (*Ber.*, 1902, **35**, 2172—2184. Compare

Abstr., 1898, i, 447—449).—Attempts to condense ethyl cuminylidenemalonate and ethyl β-aminocrotonate in mol. proportion failed to give a definite product. On heating 1 mol. of the former, however, with 2 mols. of the latter for 12 hours at 140—155° in a vacuum of 30—50 mm., the *substance*,

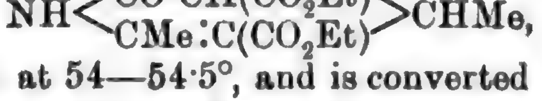


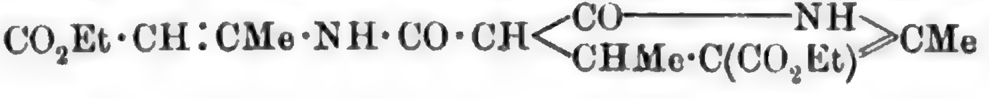
$$CO_2Et\cdot CH{:}CMe\cdot NH\cdot CO\cdot CH<\begin{array}{l}CO\cdot NH\cdot CMe\\CH(C_6H_4Pr^\beta)\end{array}>C\cdot CO_2Et,$$

is obtained; it separates from alcohol in small, white crystals, melts at about 166—168°, and when heated with 20 per cent. hydrochloric acid at 110—120°, or boiled with acetic anhydride containing sodium acetate, is hydrolysed to *ethyl* 4-iso*propylphenyldihydro-2-picolone-5-carboxylate*,  $NH<\begin{array}{l}CO\text{———}CH_2\\CMe{:}C(CO_2Et)\end{array}>CH\cdot C_6H_4Pr^\beta$; the latter is obtained from alcohol in white crystals and melts at 182—183°.

When ethyl 4-phenyldihydro-2-picolone-3:5-dicarboxylate (ethyl 6-oxy-4-phenyl-2-methyltetrahydropyridine-3:5-dicarboxylate) is rapidly hydrolysed by being dropped into a boiling 8 per cent. solution of sodium hydroxide, it gives 4-*phenyldihydro-2-picolone-5-carboxylic acid*,  $NH<\begin{array}{l}CO\text{———}CH_2\\CMe{:}C(CO_2H)\end{array}>CHPh$, which separates from alcohol in white crystals, melts and decomposes at 189—190°, and forms a white, anhydrous *silver* salt; on being heated with 20 per cent. hydrochloric acid for 8 hours at 100°, the acid is converted into γ-acetyl-β-phenylbutyric acid, and by simple melting is transformed, with loss of carbon dioxide, into 4-*phenyldihydro-2-picolone*,  $NH<\begin{array}{l}CO{-}CH_2\\CMe{:}CH\end{array}>CHPh$, which crystallises from chloroform or dilute acetic acid and melts and decomposes at 271—273°.

If in heating ethyl cuminylidenemalonate with ethyl β-aminocrotonate in a vacuum the temperature rises above 160°, considerable quantities of ethyl 5:7:4-trihydroxy-2-methylquinoline-6-carboxylate are formed (compare Knoevenagel and Fries, Abstr., 1898, i, 448).

Ethyl ethylidenemalonate (1 mol.), and ethyl β-aminocrotonate (1 mol.), readily combine at the ordinary temperature to form *ethyl dihydro-2-lutidone-*3:5-*dicarboxylate* (*ethyl* 2-*oxy*-4:6-*dimethyltetrahydropyridine*-3:5-*dicarboxylate*,  $NH<\begin{array}{l}CO\cdot CH(CO_2Et)\\CMe{:}C(CO_2Et)\end{array}>CHMe$, which crystallises from ether, melts at 54—54·5°, and is converted by 20 per cent. hydrochloric acid at 110—115° into *β-methyl-δ-pentanone-αα-dicarboxylic acid*, $CH_3\cdot CO\cdot CH_2\cdot CHMe\cdot CH(CO_2H)_2$; this is a colourless oil, easily soluble in water, which yields a stable *silver* salt, a *diethyl* salt boiling at 150—170° under 15 mm. pressure, and loses carbon dioxide when heated at 120°, giving γ-acetyl-β-methylbutyric acid. The latter boils at 153—154° under 11 mm. pressure (von Schilling, *Diss.*, Halle, 1899, gives 141° under 15 mm. pressure), and forms an *ethyl* salt boiling at 110—111° under 13 mm. pressure.

On heating ethyl ethylidenemalonate with ethyl β-aminocrotonate for 6 hours at 120—140° in a vacuum, the principal product is the *ester*,  $CO_2Et\cdot CH{:}CMe\cdot NH\cdot CO\cdot CH<\begin{array}{l}CO\text{————}NH\\CHMe\cdot C(CO_2Et)\end{array}>CMe$; it crystallises from alcohol, melts at 155—157°, and is hydrolysed by 20 per cent. hydrochloric acid at 100° to a *substance* melting at 196—197° (probably *ethyl 4-methyldihydro-2-picolone-5-carboxylate*). W. A. D.

Some Derivatives of 2-Picoline (Nitro- and Amino-stilbazoles). By KARL FEIST (*Arch. Pharm.*, 1902, **240**, 244—257).—Unlike chloral (Einhorn, Abstr., 1892, 75), acetaldehyde and benzaldehyde do not condense with α-picoline when heated with this substance and some amyl acetate even at 160°. The former does not even react in the presence of zinc chloride at 200°; benaldehyde, however, does react in these circumstances, forming stilbazole,

$$C_5NH_4\cdot CH{:}CH\cdot C_6H_5,$$

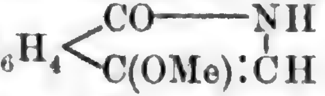
(Baurath, Abstr., 1888, 65, 608). Bromal and butylchloral do not react with α-picoline.

The nitrobenzaldehydes, like benzaldehyde, condense with α-picoline to form nitrostilbazoles, $C_5NH_4\cdot CH{:}CH\cdot C_6H_4\cdot NO_2$ (Abstr., 1901, i, 290). These are reduced by zinc and hydrochloric acid to oily *aminostilbazoles*, $C_5NH_4\cdot CH{:}CH\cdot C_6H_4\cdot NH_2$. The last substances are di-acid bases, but their hydrochlorides (which melt at 250—254°, 240°, and 260° in the case of the ortho-, meta- (with $2H_2O$), and para-isomerides respectively) lose hydrogen chloride at 100°; in the case of the meta-compound, a *dibromo*-additive product,

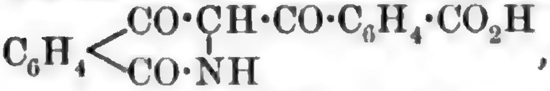
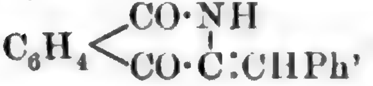
$$C_5NH_4\cdot CHBr\cdot CHBr\cdot C_6H_4\cdot NH_2,$$

was prepared, and with hydrochloric acid this forms only a monohydrochloride melting at 86—96°, which is partly decomposed by water. C. F. B.

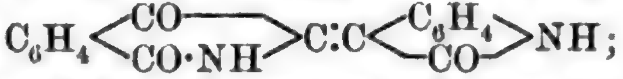
4-Hydroxy*iso*carbostyril. II. By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1902, **35**, 2421—2430. Compare Abstr., 1900, i, 359).—4-Hydroxy*iso*carbostyril is best obtained from methyl 4-hydroxy*iso*carbostyrilcarboxylate (prepared from ethyl phthalylaminoacetate), by boiling it with dilute sulphuric acid (compare *loc. cit.*).

4-Methoxyisocarbostyril,  $C_6H_4<\begin{array}{l}CO\text{———}NH\\ C(OMe){:}CH\end{array}$, is prepared from hydroxy*iso*carbostyril by heating with sodium methoxide and methyl iodide at 100°; it crystallises in needles melting at 171° and, when boiled with phosphorus oxychloride, is converted into chloromethoxy*iso*quinoline (m. p. 77°).

By the action of fuming nitric acid, hydroxy*iso*carbostyril is converted into phthaloneimide (m. p. 224°).

The *phthalide* of hydroxy*iso*carbostyril is formed on heating the latter with phthalic anhydride at 240°; it crystallises in flattened, orange needles melting at 314°, and is decomposed into its constituents by warming with concentrated potassium hydroxide; by cautious treatment with alkalis, it yields *hydroxyisocarbostyrilphthaloylic acid*,  $C_6H_4<\begin{array}{l}CO\cdot CH\cdot CO\cdot C_6H_4\cdot CO_2H\\ CO\cdot NH\end{array}$, forming pale yellow leaflets which do not melt at 265°. On heating hydroxy*iso*carbostyril and benzaldehyde in the presence of a trace of piperidine, a *benzylidene* derivative,  $C_6H_4<\begin{array}{l}CO\cdot NH\\ CO\cdot C{:}CHPh\end{array}$, is formed which exists in two forms, one crystallising in small, soluble, yellow prisms melting at 193—194°, the other crystallising in lemon-yellow needles melting at 165°, and when heated at 170° changing into the other form.

When hydroxy*iso*carbostyril is heated with isatin at 210°, a substance is formed which is probably *carbindirubin*,



$$C_6H_4<\begin{matrix}CO\text{——}\\CO\cdot NH\end{matrix}>C{:}C<\begin{matrix}C_6H_4\\CO\end{matrix}>NH;$$

it crystallises in reddish-brown needles melting at 297—299°.

On cautiously oxidising hydroxy*iso*carbostyril in solution in hydrochloric acid with potassium dichromate, dihydrocarbindigo is obtained as orange-yellow, microscopic needles, identical with the product of the reduction of carbindigo. Carbindigo is best prepared by oxidising hydroxy*iso*carbostyril with hydrogen peroxide, and is also formed when the latter is heated at 210° with phthaloneimide; when its alkaline solution is boiled with free access of air, it is oxidised, ammonia and phthalic acid being formed; on reduction with hydriodic acid and red phosphorus, a little soluble substance, $C_{18}H_{12}O_3N_2$, is obtained, which crystallises in yellowish needles darkening at 300° and melting at 390—395°.

Molecular weight determinations of carbindigo in boiling nitrobenzene confirm the dimolecular formula, $C_{18}H_{10}O_4N_2$, previously ascribed to it (*loc. cit.*). K. J. P. O.

A New Mode of Isomerism of Asymmetric Nitrogen.

By EDGAR WEDEKIND (*Compt. rend.*, 1902, **134**, 1356—1359).—Compounds containing two asymmetric carbon atoms seem to be capable of existing in stereoisomeric forms differing in chemical properties and produced by different reactions.

Ethyl ethylenebis-1-*tetrahydroisoquinoline*-1-*acetate di-iodide*,

$$C_2H_4[C_9NH_{10}(CH_2\cdot CO_2Et)I]_2,$$

exists in two isomeric forms according as to whether it is produced from ethyl tetrahydro*iso*quinolyl acetate, $C_9NH_{10}\cdot CH_2\cdot CO_2Et$, and ethylene di-iodide, or from ethyl iodoacetate and *ethylenebistetrahydroisoquinoline*, $C_2H_4(C_9NH_{10})_2$.

The isomeride obtained by the first process is the more stable; it is produced by heating its generators until a homogeneous mixture is formed and allowing the product to solidify. When crystallised from alcohol, it separates in plates melting at 168—169°.

The labile isomeride formed by heating ethylenebistetrahydro*iso*quinoline with excess of ethyl iodoacetate at 50° is obtained as a yellow, pulverulent substance decomposing at 52° with the evolution of ethyl iodoacetate. This decomposition also takes place either on allowing the di-iodide to remain for some time at the ordinary temperature or by warming it with water; under these conditions, a monoiodide, $C_9NH_{10}\cdot C_2H_4\cdot C_9NH_{10}I\cdot CH_2\cdot CO_2Et$, is produced, this salt melting at 158°.

The ethylenebistetrahydro*iso*quinoline required for this preparation is obtained by mixing together ethylene dibromide and tetrahydro*iso*quinoline in the theoretical proportion. After 12 hours, the mixture is treated with ether in the presence of alcohol and sodium carbonate;

the base is isolated on evaporating off the solvent and crystallised from petroleum. It forms almost colourless crystals and melts at 98°.

G. T. M.

Action of Alkalis on Phenanthridine and Acridine Methiodides.

By Amé Pictet and E. Patry (*Ber.*, 1902, **35**, 2534—2537).—The methiodides of phenanthridine and acridine, when treated with alkalis, behave in a similar manner to quinoline and pyridine methiodides (see Decker, Abstr., 1892, 879). Phenanthridine methiodide, when treated with sodium hydroxide, yields phenanthridine methohydroxide (see Abstr., 1891, 837), which, when distilled with steam, gives the volatile 10-methyldihydrophenanthridine (Ankersmit, *Dissertation*, Bern, 1891) and leaves 10-methylphenanthridone (Abstr., 1893, i, 658).

Acridine methiodide yields analogous products. N-*Methyldihydroacridine* separates from water in compact crystals, melts at 96°, is volatile with steam, and is oxidised in air to 10-methylacridone.

R. H. P.

Isomeride of Quinophthalone.

By Alexander Eibner and H. Merkel (*Ber.*, 1902, **35**, 2297—2301. Compare Abstr., 1901, i, 611).—An isomeride of quinophthalone is produced when phthalic anhydride is heated with quinaldine at 100—160°, the yield varying from 10—20 per cent., according to the temperature; this compound crystallises in monoclinic, orange-yellow tablets and melts at 186°. It is converted into quinophthalone by being heated with benzaldehyde, or heated alone at 240—250° for three hours; when heated at 100° with fuming sulphuric acid, it yields the same derivative as quinophthalone. In its reactions, it differs considerably from the isomeric compound. Alcoholic ammonia, which converts quinophthalone into α-quinophthaline, decomposes the new isomeride, yielding quinaldine and phthalamide. Aniline yields quinaldine and phthalanil. Phenylhydrazine yields phthalylphenylhydrazine and quinaldine. Hydroxylamine also yields quinaldine together with a small amount of a red substance which is probably a hydroxylamine derivative of quinaldine. Bromine converts the new isomeride into a dibromo-derivative, $C_{18}H_{11}O_2NBr_2$, which crystallises in silky needles melting indefinitely at about 200°; this substance is reconverted into the original compound when boiled with ammonia or aqueous soda, whilst aniline converts it into phthalanil. A. H.

Action of Ethyl β-Chloroacetoacetate on Diazo-chlorides.

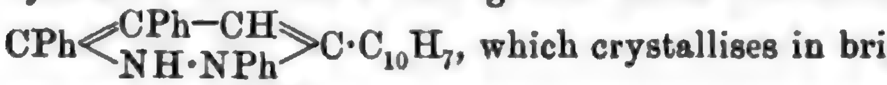
By G. Favrel (*Compt. rend.*, 1892, **134**, 1312—1313).—By the action of ethyl β-chloroacetoacetate on an aqueous solution of diazobenzene chloride, yellowish, voluminous crystals are obtained of *ethyl chloroglyoxylate phenylhydrazone*, $NHPh\cdot N:CCl\cdot CO_2Et$, which melts at 80—81°. Using diazo-*p*-toluene chloride, *ethyl chloro-oxalate*-p-*tolyl hydrazone* is obtained which melts at 103—104°; the corresponding o-*tolylhydrazone* melts at 74—75°.

The action is similar to that of ethyl methylacetoacetate and ethyl ethylacetoacetate studied by Japp and Klingemann (Proc., 1887, **3**, 142).

J. McC.

Action of Phenylhydrazine and of Phenylmethylhydrazine on α-β-Dichloro-*p*-methylstyrene. By FRANZ KUNCKELL and FRANZ VOSSEN (*Ber.*, 1902, **35**, 2291—2294).—Phenylhydrazine reacts with α-β-dichloro-*p*-methylstyrene at the temperature of boiling water; the chlorine atoms are replaced by the phenylhydrazine residues, and then oxidation occurs at the expense of the excess of hydrazine, so that the final product is Müller and Pechmann's *p*-tolylglyoxalosazone (Abstr., 1890, i, 51), the hydrochloride of which melts at 155°. α-Phenylmethylhydrazine reacts in a similar manner, yielding p-*tolylglyoxal-dimethylphenylhydrazone*, $C_6H_4Me\cdot C(:N\cdot NMePh)\cdot CH:N\cdot NMePh$, which crystallises in yellowish needles melting at 208° and readily soluble in benzene or alcohol. J. J. S.

Action of Phenylhydrazine on αδ-Diketones. By ALEXANDER SMITH and HERBERT N. MCCOY (*Ber.*, 1902, **35**, 2169—2171).—Purified acetonylacetone*bis*phenylhydrazone, contrary to previous statements, can be exposed to the air for eighteen months without resinifying. *Bimolecular acetonylacetone monophenylhydrazone*, $(C_{12}H_{14}N_2)_2$, is obtained on adding hydrochloric acid to an alcoholic solution of equal weights of phenylhydrazine and acetonylacetone, or mol. proportions of acetonylacetone and its diphenylhydrazone; it crystallises from alcohol in colourless prisms, melts at 175·5°, and by cold concentrated hydrochloric acid is converted into an isomeric *substance* which is much less soluble in alcohol, forms rectangular plates, and melts at 188°.

Desyl-β-acetonaphthone (Abstr., 1900, i, 38) interacts with phenylhydrazine dissolved in hot glacial acetic acid to form the *pyridazine*,  $CPh<\begin{matrix}CPh-CH\\NH\cdot NPh\end{matrix}>C\cdot C_{10}H_7$, which crystallises in bright yellow needles and melts at 192°.

Desyl-α-acetonaphthone, under the same conditions, is not affected. W. A. D.

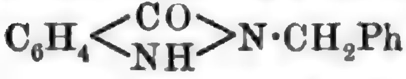
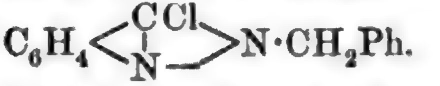
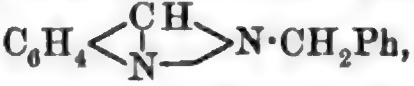
2:6-Dibromo-*p*-phenylenedi-imine. By C. LORING JACKSON and DANIEL F. CALHANE (*Ber.*, 1902, **35**, 2495—2496).—Dibromo-*p*-phenylenediamine is converted by bromine into a green salt, which yields with alkalis a brownish-red base. This salt, which is decomposed both by water and alcohol, appears to be 2 : 6-*dibromo*-p-*phenylenedi-imine hydrobromide*, $C_6H_2Br_2(NH)_2,HBr$. *p*-Phenylenediamine undergoes a similar reaction with bromine, a p-*phenylenedi-imine hydrobromide* being formed as a dark blue salt which yields a brownish-red base free from bromine. *o*-Phenylenediamine yields even less stable compounds than the para-derivative, whilst the *m*-compound reacts differently.

p-Phenylenedi-imine appears to have been obtained by Heucke (*Annalen*, 1889, **255**, 193), who, however, ascribed to it a higher molecular weight. A. H.

Some New Indazole Derivatives. By EMIL FISCHER and RICHARD BLOCHMANN (*Ber.*, 1902, **35**, 2315—2319).—*Benzylidene-o-hydrazinobenzoic acid*, $CO_2H\cdot C_6H_4\cdot NH\cdot N:CHPh$, obtained by adding benzaldehyde to an aqueous solution of *o*-hydrazinobenzoic acid at 50°, crystallises from ether in small, sulphur-yellow needles, sinters at

219°, and melts at 227—228° (corr.). When reduced with sodium amalgam, it gives *β-benzyl-o-hydrazinobenzoic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot NH\cdot CH_2Ph,$$

which crystallises from alcohol, on diluting with water, in slender needles, melts and decomposes at 134° (corr.), and is converted by warm alcoholic hydrogen chloride or glacial acetic acid into the *anhydride*,  $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>N\cdot CH_2Ph$; this crystallises from alcohol on dilution in nearly colourless needles, melts at 180·5° (corr.), and is converted by an excess of phosphorus oxychloride into *3-chloro-2-benzylindazole*,  $C_6H_4<\begin{matrix}CCl\\ \vert \\ N\end{matrix}>N\cdot CH_2Ph$. The latter is purified by distillation under 0·25 mm. pressure, when it boils at about 132—134° (corr.); it then crystallises from light petroleum in small, colourless prisms melting at 47·5° (corr.). *2-Benzylindazole*,  $C_6H_4<\begin{matrix}CH\\ \vert \\ N\end{matrix}>N\cdot CH_2Ph$, obtained by reduction with zinc dust and hydrochloric acid, crystallises from light petroleum in well-formed prisms and melts at 73° (corr.). The *picrate* melts at 167° (corr.).

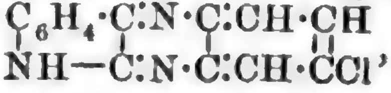
W. A. D.

Some Salts of Antipyrine. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1902, [iii], 27, 612—615).—Antipyrine *hydrochloride*, obtained by concentrating on the water-bath a solution of antipyrine in concentrated aqueous hydrochloric acid with addition of alcohol, forms thick, tabular crystals melting at 158—160°; it is very deliquescent, very soluble in water, less so in absolute alcohol, very sparingly so in ether or benzene. The salt is hydrolysed in aqueous solution, and the amount dissolved can be readily estimated by titration with alkali, using phenolphthalein as indicator.

Antipyrine hydrochloride, although almost insoluble in benzene, is fairly soluble in a boiling mixture of benzene and absolute alcohol. From this solution, it crystallises in flat, elongated prisms which contain 1 mol. of benzene of crystallisation. It is very soluble in water with liberation of benzene.

If a benzene solution containing mol. proportions of antipyrine and *d*-camphorsulphonic acid is evaporated and kept in the cold, crystals of *antipyrine* d-*camphorsulphonate* are obtained; it is not deliquescent, but is very soluble in water with strongly acid reaction. The salt is best recrystallised from a mixture of acetone and absolute alcohol.

A. F.

Isatin. By A. KORCZYNSKI and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1902, 245—260. Compare Abstr., 1901, 347, 415, 416, 615).—*a-2- (or 3)-Chloroindophenazine*,  $\begin{matrix}C_6H_4\cdot C{:}N\cdot C{:}CH\cdot CH\\ \vert \qquad \vert \qquad \vert \qquad \Vert\\ NH-C{:}N\cdot C{:}CH\cdot CCl\end{matrix}$, formed by boiling *p*-chloro-*o*-phenylenediamine with isatin in acetic acid solution, crystallises from alcohol in light yellow needles or scales, is easily soluble in acetone or chloroform, and melts above 300°. On addition of ammoniacal silver nitrate solution, the alcoholic solution yields a red precipitate. On boiling with glacial acetic acid, an *acetyl* derivative is formed, which is easily soluble in acetone, benzene, ether, or chloroform, moderately so in alcohol, from which it crystallises in white needles melting at 208°. By condensation of acetylisatin with chloro-*o*-phenylenediamine hydrochloride in hot acetic acid solution in presence of sodium acetate, β-2- (or 3)-chloroindophenazine and two isomeric chlorohydroxyacetylaminophenylquinoxalines are formed.

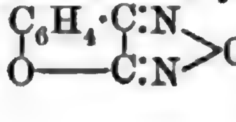
β-2- (or 3)-*Chloroindophenazine* is soluble with difficulty in acetic acid, very slightly in alcohol or ether, crystallises in yellowish needles, and melts at 310°. β-6- (or 7)-*Chloro-3-hydroxy-2-o-aminophenylquinoxaline*, $OH\cdot C_8N_2H_3Cl\cdot C_6H_4\cdot NH_2$, easily soluble in alcohol or acetone, less so in benzene, chloroform, or ether, crystallises in orange-coloured needles and melts at 229—230°, gives a red colour on addition of ether to its solution in concentrated hydrochloric acid, and when boiled with glacial acetic acid gives β-2- (or 3)-chloroindophenazine.

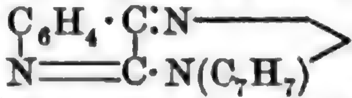
α-6- (or 7)-*chloro-3-hydroxy-2-o-aminophenylquinoxaline*, which is less soluble in organic solvents than the β-modification, forms yellowish-brown scales, melts at 265°, gives a red colour on addition of ether to the solution in concentrated hydrochloric acid, forms a white hydrochloride, and on boiling with glacial acetic acid yields α-2- (or 3)-chloroindophenazine.

9-*Bromoindophenazine*, formed by condensation of acetylbromoisatin with *o*-phenylenediamine, is sparingly soluble in alcohol, ether, acetone, benzene, or chloroform, forms yellow needles, melts at 279—280°, and yields a red precipitate on addition of ammoniacal silver nitrate to its alcoholic solution.

3-*Hydroxy*-2-m-*bromo-o-aminophenylquinoxaline*, formed together with bromoindophenazine, is easily soluble in aqueous alkalis, ether, or acetone, sparingly in alcohol, benzene, or chloroform, forms orange-coloured needles and melts at 249—250°. It yields a red colour on addition of ether to its solution in concentrated hydrochloric acid. With concentrated sodium hydroxide solution, it forms a white precipitate, probably the *sodium* derivative. The *picryl* derivative, $C_{14}H_9ON_3Br\cdot C_6H_2O_6N_3$, formed by boiling the quinoxaline with picryl chloride in alcoholic solution, is easily soluble in aqueous alkalis or acetone, sparingly in alcohol, ether, benzene, or chloroform, crystallises from acetic acid in red needles and melts at 287—288°.

3-*Hydroxy*-2-m-*bromo-o-aminophenyl*-6- (or 7)-*methylquinoxaline*, obtained from acetylbromoisatin and *o*-tolylenediamine, forms yellow-orange coloured needles and melts at 243°.

6- (or 7)-*Chloro-3-hydroxy-2-o-hydroxyphenylquinoxaline*, obtained by boiling *o*-chlorophenylenediamine with *o*-hydroxybenzoylformic acid in aqueous solution, dissolves easily in alkalis, concentrated acids, or boiling alcohol, sparingly in benzene, ether, or chloroform, crystallises in yellow needles, and melts at 286—287°. It forms a dark reddish-brown solution in sulphuric acid which, on heating, becomes yellow with formation of the *sulphonic* acid, the *sodium* salt of which crystallises with $3H_2O$. On distillation of the *barium* sulphonate, which crystallises in minute, yellowish-white needles, 2- (or 3)-*chlorocumarophenazine*,  $\left.\begin{array}{l} C_6H_4\cdot C{:}N \\ O\text{——}C{:}N \end{array}\right> C_6H_3Cl$, is obtained, which crystallises in white needles, is easily soluble in alcohol, benzene, or chloroform, and melts at 149—150°. Its solutions have a faintly green fluorescence.

5-Tolyl-ψ-indophenazine,  $\begin{array}{l} C_6H_4\cdot C{:}N \\ N{=\!=}C\cdot N(C_7H_7) \end{array} > C_6H_4$, obtained from isatin and *o*-amino-*p*-methyldiphenylamine, is easily soluble in boiling alcohol, less so in benzene or chloroform; in concentrated acids, it forms yellow or reddish-brown solutions, crystallises in glistening, brownish-red needles, and melts at 255—255·5°. The hydrochloride, formed by passing hydrogen chloride through its solution in benzene, is a yellow, crystalline powder which gives off hydrogen chloride when dry. *9-Bromo-5-tolyl-ψ-indophenazine*, obtained by using bromoisatin, dissolves in acids with a yellow coloration, easily in boiling alcohol, less readily in benzene, chloroform, or acetone, with difficulty in ether, crystallises in brownish-red needles, and melts at 290—291°.

The *benzyl* ether of isatinoxime, whether obtained by the action of benzyl chloride on the silver salt of isatinoxime or by the condensation of isatin with α-benzylhydroxylamine, dissolves easily in alcohol, acetone, benzene, or ether, sparingly in alkalis, crystallises in yellow needles, and melts at 168·5—169°. The alcoholic solution yields a red precipitate on addition of ammoniacal silver nitrate. The ethers of isatinoxime made from the silver salt have therefore the grouping C·O·R. *Bromoisatinoxime benzyl ether*, made from bromoisatin and α-benzylhydroxylamine, forms yellow needles easily soluble in boiling alcohol, acetone, benzene, or chloroform, and melts at 200°.

Chloroisatinoxime benzyl ether forms yellow needles soluble with difficulty in alcohol or ether, more easily in benzene or chloroform, and melts at 224·5°.

Nitroisatinoxime benzyl ether forms golden-yellow scales soluble with difficulty in alcohol, more easily in acetone or benzene, and melts at 234—235°.

The spectra of isatin, chloroisatin, and methylisatin show a well-defined absorption band in the region of K^β and a strong end absorption. Nitroisatin and acetylisatin show no characteristic band; this may be due to their existence in solution as isatic acids, as sodium isatate shows a similar spectrum and both nitro- and acetyl-isatin easily form quinoxalines. Indophenazine and chloroindophenazine show no characteristic absorption bands, but 5-tolyl-ψ-indophenazine and 5-methyl-ψ-indophenazine show two very distinct bands beyond the thallium line. G. Y.

Intramolecular Rearrangement of Atoms in Azoxybenzene and its Derivatives.

By H. M. Knipscheer (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, **5**, 51—53. Compare *Ber.*, 1885, **18**, 1405).—The isomeric change of azoxybenzene and its derivatives into hydroxyazobenzenes, takes place with formation of the *para*- and *ortho*-isomerides on heating at 200°, with formation of the *ortho*-isomeride only on exposure to direct sunlight or, in the case of azoxybenzene, on heating with acetic anhydride at 200°.

The action of acetyl chloride on azoxybenzene leads to the formation of di-*p*-chloroazobenzene and *p*-chloroacetanilide; of benzoyl chloride and of phosphorus pentachloride, to the formation of azobenzene, in the latter case with evolution of chlorine; and of aluminium chloride to the formation of *p*-chloroazobenzene.

The isomeric change was not brought about by the action of butyryl chloride, phosphorus oxychloride, phosphoric acid, aqueous sodium hydroxide, copper oxide, zinc oxide, or zinc carbonate.

Azoxybenzene purified by heating with Beckmann's mixture at 150—180°, is perfectly white. G. Y.

Azoxybenzylidene Bases. By FRIEDRICH J. ALWAY (*Ber.*, 1902, **35**, 2434—2438).—p-*Azoxybenzylideneaniline*, $ON_2(C_6H_4\cdot CH{:}NPh)_2$, can be prepared from *p*-azoxybenzaldehyde and aniline, or by adding solid sodium hydroxide to a boiling alcoholic solution of *p*-nitrobenzylaniline, or by boiling benzyl chloride (1 mol.) with aniline (6 mols.), adding alcohol and then sodium hydroxide; the yield represents 75 per cent. of the theoretical; this substance crystallises in golden-yellow leaflets, melting at 185°.

p-*Azoxybenzylidene*-o-*toluidine*, $ON_2(C_6H_4\cdot CH{:}N\cdot C_7H_7)_2$, prepared in a similar manner, crystallises in lustrous orange leaflets melting at 182—183°; the m-*toluidine* derivative melts at 133°, and the p-*toluidine* derivative at 188—190°.

p-Azoxybenzaldehyde is formed when the above compounds are suspended in dilute nitric acid, and crystallises in long, yellow needles melting at 194—195·5° (corr.); it dissolves in sulphuric acid with an orange coloration, and on heating the solution at 120° is converted into hydroxyazo-dyes. This compound is identical with the substance (m. p. 190°), obtained by Gattermann by the electrolytic reduction of *p*-nitrobenzaldehyde (Abstr., 1897, i, 188), and with that prepared by Kirpal (m. p. 194°, Abstr., 1897, i, 520). K. J. P. O.

Azo-compounds of Acetylacetone. By CARL BÜLOW and FRITZ SCHLOTTERBECK (*Ber.*, 1902, **35**, 2187—2191).—*o*-, *m*-, and *p*-Nitrodiazobenzene will condense with acetylacetone, not only in alkaline or neutral solution, but also in a strongly acid solution. The azo-derivatives thus formed cannot be converted into acetylated hydrazones, as can other phenylazo-derivatives of acetylacetone.

Phenylazoacetylacetone is easily prepared by mixing solutions of benzenediazonium chloride, acetylacetone, and sodium acetate (compare Beyer and Claisen, Abstr., 1888, 827); it crystallises in long, yellow needles melting at 90°, and when boiled with aqueous sodium hydroxide, is converted into aniline and a *substance*, $C_{15}H_{16}O_4$, which crystallises in white needles melting at 186°.

1-Phenyl-3:5-dimethyl-4-benzeneazopyrazole was obtained by boiling an acetic acid solution of mol. proportions of phenylhydrazine and acetylacetone (compare Beyer and Claisen, *loc. cit.*); it melts at 62°.

p-*Nitrophenylazoacetylacetone*, $NO_2\cdot C_6H_4\cdot N_2\cdot CH(COMe)_2$, is prepared by mixing alkaline solutions of acetylacetone and *p*-nitro*iso*diazobenzene, or acid solutions of acetylacetone and *p*-nitrobenzenediazonium chloride; it crystallises in brownish-yellow needles, melting at 221—222°; the corresponding o-*nitro*-derivative forms yellowish-red needles melting at 180°, and the m-*nitro*-derivative orange-yellow leaflets melting at 140°. K. J. P. O

Benzene-*p*-azobenzaldehyde. By PAUL FREUNDLER (*Compt. rend.*, 1902, **134**, 1359—1361).—The reduction of a mixture of nitrobenzene and *p*-nitrobenzaldehyde, in molecular proportion, by an alcoholic solution of sodium hydroxide and zinc dust, leads to the production of a mixture of hydrazo-derivatives, which, when subsequently oxidised by yellow mercuric oxide, give rise to azobenzene and the *methyl ethers* of *benzene*-p-*azobenzaldehyde* and s.p-*azodibenzaldehyde*. The symmetrical diacetal, $N_2[C_6H_4\cdot C(OMe)_2]_2$, is separated from the other products by its sparing solubility in alcohol; it crystallises from this solvent or ether in orange-coloured flakes and melts at 118°.

s.p-*Azodibenzaldehyde*, $N_2(C_6H_4\cdot COH)_2$, obtained by hydrolysing its methyl acetal with dilute sulphuric acid, crystallises in reddish-brown flakes from amyl alcohol or nitrobenzene, but is almost insoluble in the other organic solvents. Its *diphenylhydrazone* crystallises from nitrobenzene in dark red needles melting and decomposing at 278·5°; it dissolves in concentrated sulphuric acid to a deep blue solution.

Benzene-p-*azobenzaldehyde*, prepared by hydrolysing its acetal derivative, crystallises from acetone in red leaflets and melts at 120°; it is soluble in the ordinary organic solvents, excepting light petroleum; its *phenylhydrazone* crystallises from alcohol in red needles and melts at 165—166°.

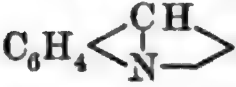
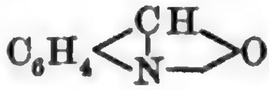
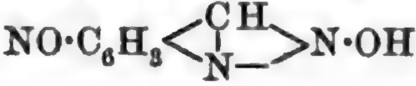
The two aldehydes may be readily sublimed without decomposition. G. T. M.

Di-*p*-nitrohydrazobenzene. By PAUL FREUNDLER and L. BÉRANGER (*Compt. rend.*, 1902, **134**, 1219—1221).—When the di-*p*-nitroazobenzene, melting at 220° and obtained by the action of nitric acid on diacetylhydrazobenzene, is reduced with ammonium sulphide, it yields a crystalline, orange-yellow compound which melts and decomposes at about 280° and agrees in its composition and properties with the di-*p*-nitrohydrazobenzene obtained by Willgerodt, Werner, and Rassow by reducing di-*p*-nitroazobenzene, except that its melting point is higher. No trace of this product can, however, be obtained by the hydrolysis of the dinitrodiacetylhydrazobenzene, which is the principal product of the nitration of diacetylhydrazobenzene. It would seem, therefore, that the yellow compound is not a true dinitrohydrazobenzene, but a tautomeric modification of it, $N_2(:C_6H_4:NO\cdot OH)_2$. The molecular compound of azobenzenediacetylhydrazobenzene previously described, yields, on nitration, only a mixture of dinitroazobenzene and dinitrodiacetylhydrazobenzene. C. H. B.

Oxime of *o*-Azidobenzaldehyde [*o*-Triazobenzaldehyde]. By EUGEN BAMBERGER and ED. DEMUTH (*Ber.*, 1902, **35**, 1885—1896. Compare Abstr., 1901, i, 392, 621).—When *o*-triazobenzaldoxime is dissolved in aqueous sodium hydroxide and the solution boiled for some time, the following compounds are produced: (1), a crystalline acid, $C_7H_6ON_2$; (2), an amorphous acid, $C_7H_6ON_2$; (3), a neutral substance, $C_7H_6ON_4$; (4), *o*-aminobenzaldoxime; (5), *o*-triazobenzoic acid,

$N_3\cdot C_6H_4\cdot CO_2H$; (6), anthranilic acid (?); (7), small quantities of unidentified substances.

The neutral substance, $C_7H_6ON_4$, isomeric with *o*-triazobenzaldoxime, is shown to be *o-triazobenzamide*, $N_3\cdot C_6H_4\cdot CO\cdot NH_2$, and its formation is of interest as showing that the Beckmann type of isomeric change may take place under the influence of alkalis; it crystallises from dilute sodium hydroxide in long, colourless, silky needles, melts at 135·5—136°, and can be synthesised from *o*-triazobenzoic acid by the action of phosphorus pentachloride and then of ammonia.

The crystalline acid, $C_7H_6ON_2$, is shown to be 2-*hydroxyindazole*,  $C_6H_4{<}\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}{>}N\cdot OH$, and its formation is analogous to that of anthranil, formulated as  $C_6H_4{<}\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}{>}O$, from *o*-triazobenzaldehyde (Abstr., 1901, 95 and 127); it may be regarded as the oxime of anthranil; it crystallises from water in white needles, and from ether in glistening prisms, melts at 139—139·5°, and dissolves in alkali carbonates and hydrogen carbonates. The acid *silver* salt, $C_7H_5ON_2Ag,C_7H_6ON_2$, forms a white, crystalline precipitate, detonates when heated, becomes brown at 190°, sinters, and then melts and decomposes at 202·5—203·5°. *Nitroso-2-hydroxyindazole*,  $NO\cdot C_6H_3{<}\begin{smallmatrix}CH\\ |\\ N\end{smallmatrix}{>}N\cdot OH$, crystallises from water in red, silky needles, dissolves readily in alcohol or acetone and in alkalis, hydroxides, and ammonia, sinters at 156°, becomes dark and explodes at 167°, and gives Liebermann's reaction. Hydroxyindazole is reduced by tin and hydrochloric acid or by zinc dust and ammonium chloride to E. Fischer's indazole.

The amorphous acid, $C_7H_6ON_2$, is possibly a polymerised hydroxyindazole.

T. M. L.

The Properties of Proteids of combining with Acids.

By Ladislaus von Rhorer (*Pflüger's Archiv*, 1902, **90**, 368—388).—In the estimation of equivalent quantities of proteid and acid the precipitation method is the best. The results obtained are independent of the nature of the precipitant and of excess of acid. The fact that porteids are precipitable by alkaloid reagents from acid solutions only, is due to slight dissociation, and therefore depends on the basic character of proteids. Proteids are amphoteric electrolytes.

W. D. H.

The Chemical Action between Proteids and Aniline Dyes.

By Martin Heidenhain (*Pflüger's Archiv*, 1902, **90**, 115—230).—The reaction between proteids and aniline dyes is regarded as more of a chemical than of a simply physical nature. Proteids can react with both bases and acids, and can thus combine with both acidic and basic dyes. As a rule, with a special proteid either the acidic or basic character is the more pronounced, and there is thus a greater tendency to form compounds with basic or acidic dyes.

The action of aromatic sulphonic acids on proteids is largely a function of the relative acidity of the acid. The greater the strength of the acid, the more readily are the proteids precipitated. The precipitation is probably accompanied by a conversion of the proteids into acid albumins.

Although a number of neutral dye salts do not precipitate proteids, yet the free acids or bases corresponding with these salts readily form coloured precipitates. For example, egg-albumin is not precipitated by naphthol yellow S, or by indigocarmin, and yet is readily precipitated by these reagents in the presence of a little acetic acid.

The action of some 30 acidic dyes on albumin and casein under varying conditions has been studied, and the results tabulated. Feebly acidic dyes are the best reagents for the precipitation, stronger acids are not so active, owing probably to their high molecular weights. Violet black is capable of precipitating extremely dilute solutions of proteids in the presence of acetic acid. The presence of amino-groups in an acid dye tends, in most cases, to lessen the precipitating power of the dye. The most active precipitating agents are ponceau 2R and 3R, palatine-red and new coccin.

Acetic acid is capable of changing the colour of congo-red to blue, but in the presence of small amounts of serum-albumin the change in colour does not occur. Aminoazosulphonic acids combine with proteids even in the presence of a large excess of acetic acid, and certain of the products formed dissolve in glacial acetic acid without undergoing decomposition. The colours of the proteid compounds resemble those of the sodium salts of the dye. Varying amounts of dye are taken up by the proteid, and the colour of the product becomes darker as the amount of dye increases. When only minute quantities of the acid dye are employed, the compound remains in solution, but a slight increase in the amount of dye precipitates the proteid in the form of a coloured albumin sulphonate.

Anthracene-blue and alizarin-brown are capable of precipitating certain proteids. In some cases, the amount of mineral matter present in the proteid affects the precipitation.

Basic dyes are also capable of precipitating proteids, forming coloured precipitates which are presumably salts of the dye base with the acidic proteid. If the base is a feeble one, then serum-albumin is often capable of decomposing the dye salt, combining with the acid and setting free the colour-base. The dye salt of a stronger base is also decomposed, but both the acid and the colour-base combine with the proteid. With salts of extremely strong basic dyes, no decomposition occurs, but the proteid combines directly with the salt; that is, the salts act as partially neutralised bases, and the coloured products formed are usually thrown out of solution. Nucleic acids readily combines with basic dyes. J. J. S.

Possible Combinations of Fat and Proteid. By E. R. Posner and William J. Gies (*Amer. J. Physiol.*, 1902, 7, 331—339. Compare this vol., i, 331).—In connection with Nerking's work on fat-proteid compounds, it is concluded that many proteids (tendon-mucoid, osseomucoid, chondro-mucoid, collagen, gelatin, elastin, edestin, myosin, egg-albumin, Witte's peptone, somatose, chloralbacid) of the simple, compound, and albuminoid types, prepared by the best methods, are not 'fat proteid' compounds, nor do they bear any resemblance to lecithalbumins. W. D. H.

Action of Alkali Hydroxides on Egg-Albumin. By Carl Paal (*Ber.*, 1902, **35**, 2195—2206).

—The action of alkali hydroxides on egg-albumin has been reinvestigated, and the acids which are precipitated on neutralising the alkaline solutions have been studied.

Protalbic acid is prepared by heating albumin at 100° with 3 per cent. aqueous sodium hydroxide for one hour; during this process, ammonia is evolved, and the solid nearly entirely dissolves; on acidifying with acetic acid, the acid is precipitated, and is freed from salts by dialysis. When freed from water by washing with alcohol, and subsequent drying, it forms a white powder, easily soluble in aqueous acetone or acetic acid, and both in alkalis and acids. A series of analyses of the acid and its salts gives C = 53·5—54, H = 7·3—7·5, N = 14·3—14·6 per cent; a small quantity of sulphur is also present. The *sodium* salt, prepared by dissolving the acid in excess of sodium hydroxide, and removing the excess of alkali by dialysis, is a white, amorphous powder; the *potassium*, *calcium*, and *barium* salts are similar; the *zinc*, *ferric*, *mercuric*, and *silver* salts, prepared by precipitation, were all analysed.

Lysalbic acid is contained in the mother liquors, from which protalbic acid has separated, and is isolated by evaporating the solution to a small bulk, and then acidifying with sulphuric acid; it may be purified by pouring its concentrated aqueous solution into alcohol, and is a white powder forming an acid solution and giving the biuret reaction. Its composition is C = 50·5—51·2, H = 6·6—6·9, N = 15·1—15·7 per cent.; a small quantity of sulphur was present; cryoscopic determinations of the mol. weight of the acid dried over sulphuric acid gave 818—838, and of the acid dried at 100°, 1171—1187. The *sodium* salt is an amorphous, soluble powder, the *ferric* salt a red powder, and the *silver* salt a yellow powder. K. J. P. O.

Action of Dilute Nitric Acid on Casein and the Formation of Hydroxyglutaric Acid. By Josef Habermann and R. Ehrenfeld (*Zeit. physiol. Chem.*, 1902, **35**, 231—245).

—When the liquid obtained by heating casein with dilute nitric acid for several hours at 70° is extracted with ether and the solvent distilled off, there is left a crystalline residue, consisting chiefly of oxalic acid, but containing also hydroxyglutaric acid, which was purified by conversion into its zinc salt and recrystallisation of the latter, and a yellow, oily substance which accumulated in the mother liquors from the zinc hydroxyglutarate, and was eventually obtained in the form of reddish-yellow, crystalline nodules. This is volatile in steam, and is probably a nitro-derivative of a higher fatty acid. The ethereal residue referred to had a strong odour of leucic acid, but this, if present, could not be isolated. The original liquid, when distilled with steam, furnished a mixture of acetic and benzoic acids. No xanthoproteic acid was formed. T. A. H.

Fibroin and Gelatin of Silk. By EMIL FISCHER and ALADAR SKITA (*Zeit. physiol. Chem.*, 1902, **35**, 221—226. Compare Wetzel, Abstr., 1899, i, 466; Fischer and Skita, Abstr., 1901, i, 783).—In addition to the monoamino-acids previously obtained by the hydrolysis of silk-fibroin with hydrochloric acid, the authors have now isolated by their usual method (Abstr., 1901, i, 192) serine 1·6 per cent., arginine 1 per cent., and probably histidine and lysine. When silk-gelatin is hydrolysed by boiling with dilute sulphuric acid, there are formed tyrosine, *i*-serine, arginine 4 per cent., lysine, glycine 0·1 per cent., *d*-alanine 5 per cent., and a seventh amino-acid, not yet identified, which differs from phenylalanine in being soluble in concentrated hydrochloric acid. The methods adopted for the separation of the acids were those of Fischer and of Kossel (Abstr., 1899, i, 833).

T. A. H.

Antipeptone. II. By MAX SIEGFRIED (*Zeit. physiol. Chem.*, 1902, **35**, 164—191. Compare Abstr., 1901, i, 57).—Antipeptone, although readily hydrolysed by alkalis, is relatively stable in the presence of trypsin.

The two acids previously described are most readily separated by the aid of their iron compounds. *β-Antipeptone*, $C_{11}H_{19}O_5N_3$, which is first precipitated as its iron compound, is a monobasic acid and has $[\alpha]_D$ − 21·43° at 16°. *α-Antipeptone*, $C_{10}H_{17}O_5N_3$, is also a monobasic acid; it yields an iron derivative which is more readily soluble than that of its isomeride, and has $[\alpha]_D$ −18·45 or −19·69. Both compounds are snow-white powders only sparingly soluble in 96 per cent. alcohol, but readily so in phenol. The solutions have an acid reduction, whereas solutions of the sodium and barium salts give an alkaline reaction. They slowly decompose when heated at 100°. With Millon's reagent, Molisch's reagent, lead acetate, metaphosphoric acid, potassium ferrocyanide, or acetic acid, no characteristic reactions are given. They both give the biuret test and also yield precipitates with picric acid, mercuric chloride, or phosphotungstic acid. Decomposition of *α*-antipeptone with stannous chloride and hydrochloric acid gives rise to lysatinine, aminosuccinic acid, and lysine; the *β*-compound when treated similarly yields the same bases and glutamic acid. Peptone prepared from gelatin has a much higher molecular weight than the antipeptones and on decomposition with stannous sulphate and sulphuric acid yields arginine, lysine, glutamic acid, and glycine.

J. J. S.

Hydrogenases of the Blood and the Catalytic Properties of Fibrin. By M. EMM. POZZI-ESCOT (*Bull. Soc. Chim.*, 1902, [iii], **27**, 459—460).—When the action of fibrin which has been digested in glycerol or alcohol for 48 hours is compared with that of fibrin obtained from blood and rapidly washed with water, with respect to its power of liberating oxygen from hydrogen peroxide, it is found that the fibrin which has been obtained in the former manner is less active than the latter, and that the liquid in which the fibrin was digested exhibits the properties of the hydrogenases. From this, the author concludes that the above property of fibrin is due to its retention of hydrogenising diastases. A. F.

Influence of Heat on Enzymes. By S. P. Beebe (*Amer. J. Physiol.*, 1902, 7, 295—300).—No evidence was obtained of marked changes in the physical character of enzyme solutions which had been subjected to a temperature of about 40°. W. D. H.

The Inactivity of Lipase towards the Salts of Certain Acid Ethers considered in the Light of the Theory of Electrolytic Dissociation. By J. H. Kastle (*Amer. Chem. J.*, 1902, 27, 481—486).—Diethyl fumarate, diethyl oxalate, diethyl phthalate, ethyl oxamate, and ethyl *p*-sulphoaminobenzoate are easily hydrolysed by lipase, but no hydrolysis takes place with sodium ethyl fumarate, potassium ethyl oxalate, barium ethyl phthalate, diethyl *p*-nitrosulphobenzoate, barium or potassium *p*-sulphonitrobenzoate, ethyl *p*-sulphobenzoate, or barium or potassium ethyl sulphate.

From the results so far obtained on the hydrolysis by ferments, it appears that when the ester is electrolytically dissociated no hydrolysis takes place; this indicates that hydrolysis is preceded by combination of the hydrolyte with the enzyme and the combination cannot take place with ions, but only with undissociated molecules. J. McC.

Chemical Nature of Pepsin and other Digestive Enzymes. By Hans Friedenthal and S. Miyamota (*Chem. Centr.*, 1902, i, 1117—1118, 1169; from *Centr. Physiol.*, 15, 785—786, 16, 1).—The nucleo-proteid material precipitable from dog's gastric juice can be broken up, and the products, which contain neither proteid nor nucleic acid, have peptic activity. The substance or substances which produce the effect are not dialysable, and are therefore of high molecular weight; they contain less ash than the original material. The zymophore group of the pepsin molecule is not proteid, which is against the view expressed by Pekelharing. W. D. H.

Jacquemase, a New Reducing Diastase Extracted from the Japanese Koji, and Secreted by "Eurotium Oryzae." By M. Emm. Pozzi-Escot (*Bull. Soc. Chim.*, 1902, [iii], 27, 557—560).—The author shows that the taka diastase, extracted from koji, although possessing reducing properties, is not the same as philothion; in particular, it does not yield hydrogen sulphide with sulphur. For this new class of reducing diastases, the author proposes the name reductases. A. F.

New Diastases in Urine. By M. Emm. Pozzi-Escot (*Ann. chim. anal.*, 1902, 7, 212—213).—The author has discovered a new class of diastases which he calls "reductases." Their presence in urine may be proved by first adding an antiseptic, sodium fluoride, and then hydrogen peroxide; if "reductases" are present, the latter will be decomposed.

For further particulars, the author refers to his other papers on the subject. L. de K.

Formation of Aromatic Mercury Compounds. By Otto Dimroth (*Ber.*, 1902, **35**, 2032—2045. Compare Dimroth, Abstr., 1899, i, 154, 428; and Pesci, Abstr., 1892, 1448; 1898, i, 648).—Aromatic compounds react with great ease with mercury acetate, thus, at 110—120°, benzene yields phenylmercury acetate. On boiling benzene, containing thiophen, with mercuric acetate, the latter forms a compound, $OAc\cdot Hg\cdot C_4SH_2\cdot Hg\cdot OH$; by this means, the whole of the thiophen can be removed from benzene, whilst at the same time but very little of the benzene forms a mercury derivative.

Naphthalene forms a mixture of mercury compounds, from which only α-naphthylmercury acetate was isolated (Otto, *J. pr. Chem.*, 1870, [ii], 1, 185).

Nitrobenzene was heated with mercury acetate at 150°, and the resulting mixture treated with sodium chloride, when o-*nitrophenylmercury chloride* is obtained as yellowish leaflets melting at 181—182°, and with bromine in the presence of water, yielding *o*-bromonitrobenzene.

Aniline and an aqueous solution of mercuric acetate give mainly *p*-aminophenylmercury acetate (m. p. 166—167°), together with a small quantity of the isomeric ortho-*compound*, $NH_2\cdot C_6H_4\cdot Hg\cdot OAc$, which crystallises in leaflets melting at 158—160°; its *acetyl* derivative, prepared by the use of acetic anhydride, crystallises in small leaflets melting at 156—158°, and is converted by bromine into *o*-bromoacetanilide. On adding sodium chloride to an acetic acid solution of *o*-aminophenylmercury acetate, o-*aminophenylmercury chloride*, $NH_2\cdot C_6H_4\cdot HgCl$, is immediately formed, and crystallises in colourless leaflets; *p*-aminophenylmercury acetate, on the other hand, only yields the corresponding *chloride* in the absence of acetic acid; this chloride crystallises in leaflets melting and decomposing at 188°; in the presence of acetic acid, an insoluble, amorphous, polymeric *chloride* is obtained.

With sodium thiosulphate, *p*-aminophenylmercury acetate or chloride yields an unstable *compound*, $NH_2\cdot C_6H_4\cdot Hg\cdot S_2O_3Na$, which crystallises in lustrous leaflets melting and decomposing at 95°, and decomposes very readily on warming with water into *p*-mercurianiline, $(NH_2\cdot C_6H_4)_2Hg$, and sodium mercury thiosulphate.

The compound obtained by the action of sodium hydroxide on *p*-aminophenylmercury acetate is regarded by the author as *p*-mercuriphenylimine, $NH\colon C_6H_4\colon Hg$; on treatment with methyl iodide, it is converted into *iodomercuriphenyltrimethylammonium iodide*, $IHg\cdot C_6H_4\cdot NMe_3I$; the latter crystallises in greenish-yellow prisms melting at 139—140° and readily decomposes into mercuric iodide and *p*-mercuriphenyltrimethylammonium iodide, $Hg(C_6H_4\cdot NMe_3I)_2$.

Dimethylaniline reacts with mercuric acetate, forming *p*-dimethylaminophenylmercury acetate.

Attention is drawn to the fact that mercury derivatives of anilines, in which the mercury is attached to the nitrogen, for example, $Hg(NHPh)_2$, are immediately decomposed by hydrogen sulphide, whereas *p*-aminophenylmercury acetate, &c., are unchanged by this agent.

K. J. P. O.

Organic Chemistry.

Synthesis of Ethyl Alcohol. By P. Fritzsche (*J. pr. Chem.*, 1902, [ii], **65**, 597—600. Compare Berthelot, Abstr., 1899, i, 471).—A defence of Hennel. G. Y.

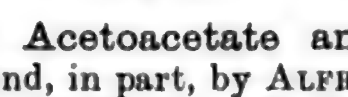
Action of Alcohols on the Sodium Compounds of other Alcohols. By Marcel Guerbet (*Compt. rend*, 1902, **135**, 172—175).—By heating together in a sealed tube to 230° a mixture of heptyl alcohol, ethyl alcohol, and sodium, there is formed *n*-nonyl alcohol (b. p. 212—214°). In the same way, a mixture of heptyl alcohol and *n*-propyl alcohol gives β-methyl-*n*-nonyl alcohol,

$$CH_3\cdot[CH_2]_6\cdot CHMe\cdot CH_2\cdot OH,$$

as a colourless oil which boils at 221—223°, and has the sp. gr. 0·8457 at 0° and 0·8333 at 15°. Its acetate is a colourless oil, with an odour resembling that of lemon; it boils at 238—240° and has the sp. gr. 0·8812 at 0° and 0·8705 at 15°. When the alcohol is heated at 250° with fused potassium hydroxide, the corresponding acid, $C_{10}H_{20}O_2$, is formed as a colourless oil which boils at 261—265°, and has a sp. gr. 0·9127 at 0°; it gives an amide which melts at 76°. The constitution of the acid was found from the oxidation products—carbon dioxide, acetic, heptoic, and octoic acids. From the constitution of the alcohol, it is evident that the condensation has taken place at the expense of the hydroxyl of the heptyl alcohol. J. McC.

Action of Selenyl Chloride on Erythritol. By Camille Chabrié and R. Jacob (*Compt. rend.*, 1902, **134**, 1507—1509).—When erythritol is heated with selenyl chloride, hydrogen chloride is given off at 68°. When the mixture is heated for an hour at 100°, a yellowish oil is obtained which does not solidify at − 15° and is easily soluble in water or alcohol. When the mixture is heated at 178°, then allowed to cool, and filtered, colourless, needle-shaped crystals separate which melt at 155°. The composition of these is represented by the formula $C_4H_6O_4Se$, from which it is evident that the erythritol has lost one mol. of water in the reaction, and two atoms of hydrogen have been replaced by the selenyl group with simultaneous production of two mols. of hydrogen chloride.

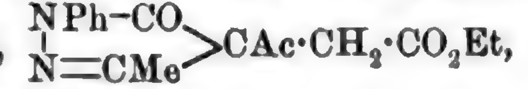
Glycol, when heated with selenyl chloride, gives off water, but inositol does not, and since the former contains only primary alcohol groups and the latter only secondary alcohol groups, it is concluded that the mol. of water is eliminated from the primary alcohol groups, and the hydrogen of the evolved hydrogen chloride from the secondary alcohol groups; consequently, the constitution of the compound produced is



$$O{<}\begin{array}{l}CH_2\cdot CH\\ CH_2\cdot CH\end{array}{>}SeO.$$

J. McC.

Ethyl Acetoacetate and its Derivatives. By Ernst von Meyer [and, in part, by Alfr. Friessner and Th. von Findeisen] (*J. pr. Chem.*, 1902, [ii], **65**, 528—533).—In the preparation of ethyl acetoacetate by the action of sodium on ethyl acetate, the amount of hydrogen evolved is almost proportional to the yield of ester. It is found impossible to increase the yield beyond 40 per cent. of the theoretical.

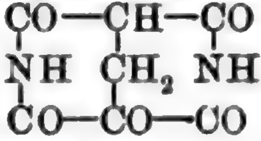
The action of *p*-toluenesulphonic chloride on ethyl sodioacetoacetate leads to the formation of sodium *p*-toluenesulphinate and ethyl α-chloroacetoacetate, and also to ethyl *p*-toluenesulphoacetoacetate, probably $C_7H_7\cdot SO_2\cdot O\cdot CMe{:}CH\cdot CO_2Et$, which reacts with unchanged ethyl sodioacetoacetate to form ethyl sodio-*p*-toluenesulphoacetoacetate, and on addition of water is decomposed into sodium *p*-toluenesulphonate and ethyl acetoacetate. Acetylation of ethyl acetylsuccinate by sodium and acetyl chloride results in the formation of ethyl *as*-diacetylsuccinate, which boils at 275° and with phenylhydrazine yields a *pyrazolone* derivative,  $\left.\begin{array}{l}\text{NPh-CO}\\ \ \ |\\ \text{N=CMe}\end{array}\right>\text{CAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, which forms white crystals and melts at 79°. G. Y.

Crystallography of Methyl Methylcamphocarboxylate, Ethyl Methylcamphocarboxylate, Methylcamphoronitrile, and Methylcamphorimide. By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], **27**, 681—683).—Methyl methylcamphocarboxylate forms monoclinic prisms [$a:b:c = 0{\cdot}70686:1:0{\cdot}6142$; $\beta = 115°$]. Ethyl methylcamphocarboxylate crystallises in rhombic prisms [$a:b:c = 0{\cdot}88213:1:0{\cdot}60063$]. Methylcamphoronitrile crystallises in rhombic prisms [$a:b:c = 0{\cdot}63707:1:0{\cdot}33636$]. Methylcamphorimide forms small crystals apparently belonging to the anorthic system. A. F.

Action of Ammonia on Halogen-substituted Malonic Acids. By O. LUTZ (*Ber.*, 1902, **35**, 2549—2554. Compare this vol., i, 596). —Bromomalonic acid can be prepared advantageously by direct bromination in acetic acid solution; the product is evaporated over sodium hydroxide in a vacuum desiccator and recrystallised from a little acetone (over sodium hydroxide) or much benzene (over paraffin) in a vacuum desiccator. Unlike the monohalogen-substituted succinic acids, chloro- and bromo-malonic acids yield aminomalonic acid, and not tartronaminic acid, when treated with ammonia. T. M. L.

α-Hydroxyglutaric Acid and the Action of Bromine on Glutaric Acid. By V. PAOLINI (*Gazzetta*, 1902, **32**, i, 402—409).—When glutaric acid is heated in a sealed tube with bromine, it yields α-bromoglutaric acid, which then splits up in two distinct ways: (1) Hydrogen bromide is given off with the formation of pentane-2 : 5-olidoic acid, and the latter becomes hydrolysed to α-hydroxyglutaric acid. (2) Part of the α-bromoglutaric acid loses carbon dioxide, giving γ-bromobutyric acid, which gives up hydrogen bromide yielding γ-butyrolactone, and this, on hydrolysis, forms succinic acid.

The dehydration of α-hydroxyglutaric acid yields pentane-2 : 5-olidoic acid and also glutaconic acid. T. H. P.

Action of Amino-bases on Ethyl Dicarboxyglutarate and of Ethyl Chloroacetate on Ethyl Dicarboxyglutaconate. By MAX GUTHZEIT and CARL JAHN (*J. pr. Chem.*, 1902, [ii], **66**, 1—15).—Ethyl dicarboxyglutarate, when treated with ammonia or aniline, yields the corresponding tetra-amide or tetra-anilide. The *tetra-amide* separates from water in white crystals and melts and evolves ammonia at 248—249°. The *di-imide*,  obtained by heating the tetra-amide under reduced pressure at 250°, crystallises from alcohol, decomposes at about 200°, and forms a crystalline *silver* salt. The *tetra-anilide* separates from alcohol as a white, crystalline powder and melts at 255—256°.

Ethyl chloroacetate reacts with the disodium derivative of ethyl dicarboxyglutaconate, forming *ethyl butenepentacarboxylate*,

$$C(CO_2Et)_2{:}CH{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CO_2Et,$$

which is a yellow, viscous oil boiling at 222—225° under 16 mm. pressure, and is split up by ammonia, yielding ethyl aminoethylenedicarboxylate and the triamide of ethanetricarboxylic acid. The ethyl aminoethylenedicarboxylate obtained by the authors melts at 56—57°, and is probably an isomeride of that obtained by Ruhemann and Morrell (Trans., 1891, **59**, 747).

Ethanetricarboxyltriamide separates from alcohol as a white, microcrystalline powder and melts and decomposes at 225°.

Ethyl butanepentacarboxylate, obtained by reducing the corresponding butene compound with zinc dust and acetic acid, is a colourless, thick oil which boils at 220—240° under 12 mm. pressure and is not split up by aqueous ammonia. R. H. P.

Reaction between Chloral Hydrate and Alkali. By WILHELM BÖTTGER and ARTHUR KÖTZ (*J. pr. Chem.*, 1902, [ii], **65**, 481—499. Compare Reicher, *Rec. trav. Chim.*, 1885, **4**, 347).—With a slight excess of alkali present at the commencement, the reaction between chloral hydrate and alkali is apparently bimolecular; the presence of slight excess of chloral hydrate diminishes the rate of reaction, which becomes unimolecular. The end of the reaction is complicated by the presence of chlorine ions. The production of hydrogen and chlorine ions in a neutral solution of chloral hydrate is caused by contact with platinised platinum foil; non-platinised platinum has little or no effect. Addition of hydrochloric acid to the solution tends to diminish the rate of the reaction. This reaction takes place also with the sodium salts of trichloroacetic, nitro-, *m*-cyano-, *m*-chloro-, *o*-chloro-, and bromo-benzoic acids and of dibromosuccinic acid, the aqueous solution becoming acid and giving the reactions of the ions, NO_2', CN', Cl', Br'.

The hydrolysis of chloroform in aqueous solution and of ethyl acetate in alkaline solution is accelerated by the presence of platinised platinum (compare Kohlrausch, Abstr., 1900, ii, 408). G. Y.

Transformation of Ketones into α-Diketones. VI. By GIACOMO PONZIO and V. BORELLI (*Gazzetta*, 1902, **32**, i, 419—424).—By the action of hydroxylamine on a dichloroketone prepared from dipropyl ketone by the successive action of phosphorus pentachloride, sodium hydroxide, and hypochlorous acid, Faworski and Desbout (Abstr., 1895, i, 496) obtained a substance melting at 129° which they regarded as propionylbutyryldioxime. This compound, however, prepared by Fileti and Ponzio (Abstr., 1897, i, 317) by the action of hydroxylamine hydrochloride on the product obtained by oxidising dipropyl ketone with nitric acid, was found to melt at 167—168°. The authors have now prepared this substance from propionylbutyryl and find that it melts at 167·5°.

Propionylbutyryl, $CH_2Me{\cdot}CO{\cdot}COPr^a$, obtained by oxidising dipropyl ketone by means of nitric acid, is a yellow liquid which boils at 147° under 732 mm. pressure and is readily volatile in steam. Its *phenylhydrazone*, $CH_2Me{\cdot}C(N_2HPh){\cdot}COPr^a$, crystallises from dilute alcohol in straw-yellow prisms melting at 91·5°.

iso*Nitrosodipropyl ketone*, $NOH{:}CEt{\cdot}COPr^a$, obtained by the action of nitrous acid on dipropyl ketone, is a dense, colourless liquid boiling at 145° under a pressure of 60 mm.

Propionylbutyryl-α-hydrazone-β-oxime crystallises from dilute alcohol in almost white prisms which melt at 135° and are soluble in ether.

T. H. P.

Formation of Ketoximes. By Luigi Francesconi and A. Milesi (*Gazzetta*, 1902, **32**, i, 425—436).—The authors have studied the reaction between acetoxime and an acid, which they find to be very rapid. In about an hour, a condition of equilibrium is reached which is independent of the nature of the acid, and is represented approximately by the equation: Acetoxime (2/3) + acid (2/3) + water = acetone (1/3) + hydroxylamine salt (1/3). These results not being in agreement with Prati's experiments (Abstr., 1895, ii, 259) on the inverse reaction to the above, the latter were repeated, the results obtained being in complete accord with those of the authors.

Experiments made with the help of methyl acetate to determine the extent to which salts of hydroxylamine undergo hydrolysis in dilute solution show that the proportion of acid set free in this manner is very slight. Conductivity measurements confirm this result.

T. H. P.

Isolation of Ketoses. II. By Carl Neuberg (*Ber.*, 1902, **35**, 2626—2633. Compare this vol., i, 264).—In phenylmethylhydrazine, the author has found a reagent which forms osazones only with the ketoses of the *i*-erythritol, adonitol, xylitol, and dulcitol series, and not with the aldoses (compare *loc. cit.*).

The solutions containing ketoses were obtained by oxidising the polyhydric alcohols either with nitric acid, sodium hypobromite, hydrogen peroxide and ferrous sulphate, or lead dioxide and hydrochloric acid.

i-*Erythrulosephenylmethylosazone*, $C_{18}H_{22}O_2N_4$, was prepared by oxidising erythritol with hydrogen peroxide and ferrous sulphate, and after neutralising and evaporating to dryness taking up the residue with alcohol and adding the hydrazine and acetic acid; the osazone forms yellowish crystals melting at 158—159°; at most, 3 grams of osazone were obtained from 12 grams of erythritol.

i-*Xyloketosephenylmethylosazone*, $C_{19}H_{24}O_3N_4$, was prepared from the product of oxidation of xylitol with lead dioxide and hydrochloric acid; it was formed in very small quantity and crystallised in yellow needles melting at 173°.

i-*Riboketosephenylmethylosazone*, $C_{19}H_{24}O_3N_4$, crystallises in slender needles, softening at 171° and melting at 175°.

i-*Tagatosephenylmethylosazone*, $C_{20}H_{26}O_4N_4$, prepared from dulcitol, melts at 148—150° and is optically inactive, as are all the osazones just described.

This method has also been used, in order to determine whether ketoses or aldoses are formed, when glycolaldehyde or "glycerose" is caused to condense to higher sugars by the action of alkalis. The sugar obtained from glycolaldehyde did not yield an osazone with phenylmethylhydrazine, but only with phenylhydrazine; thus an aldo- and not a keto-tetrose was present. The hexose obtained from "glycerose," gave a phenylmethylosazone, $C_{20}H_{26}O_4N_4$, crystallising in reddish-yellow needles melting at 158° and identical with the osazone obtained from *r*-fructose; "acrose" is then *r*-fructose.

On treating "formose," obtained from formaldehyde, in a similar manner, no hexo-osazone was produced, but a phenylmethylpentosazone, $C_{19}H_{22}O_3N_4$, which crystallised in yellow needles melting at 137° and not identical with any known pentosazone. K. J. P. O.

Two new Sugars contained in Manna, Manneotetrose, and Manninotriose. By CHARLES TANRET (*Compt. rend.*, 1902, **134**, 1586—1589).—Manna (the exudation of *Fraxinus ornus*) contains, besides mannitol, two sugars, manneotetrose and manninotriose, forming together about a sixth of the manna. To isolate these sugars, the manna is extracted with water and the mannitol precipitated with alcohol; from the mother liquors the sugars are obtained as barium compounds, which are fractionally decomposed by carbon dioxide and then fractionally crystallised from alcohol.

Manneotetrose, $C_{24}H_{42}O_{21}$, forms small, monoclinic crystals, with $4·5H_2O$, which change at 150° and melt at 167°; the hydrated sugar has $[\alpha]_D + 133·85°$, and the anhydrous $[\alpha]_D + 150°$; it does not reduce Fehling's solution. By acetic acid, it is converted into the manninotriose, above mentioned, and lævulose; the enzymes, emulsin, diastase, and invertase have a similar action. With lead acetate in the presence of ammonia, the *compound* $C_{24}H_{34}O_{22}Pb_4$ is formed as a precipitate; the *barium* derivative, $(C_{24}H_{42}O_{21})_2(BaO)_3$, is prepared by addition of baryta in the presence of alcohol to an aqueous solution. Manneotetrose is partially fermented by yeast.

Manninotriose, $C_{18}H_{32}O_{16}$, is best obtained pure by treating the mixture of manneotetrose and manninotriose, obtained from manna, with 20 per cent. acetic acid which converts the tetrose into the triose; after extracting the acid with ether, the sugar is obtained by evaporating and precipitating with alcohol; it has $[\alpha]_D + 167°$, reduces Fehling's solution, and decomposes at 150°; by mineral acids, it is converted into galactose (2 mols.) and dextrose (1 mol.). When oxidised with bromine water, it yields manninotrionic acid, $C_{18}H_{32}O_{17}$, which is hydrolysed by acids to galactose and gluconic acid.

K. J. P. O.

Betaine Aurichloride. By RICHARD WILLSTÄTTER (*Ber.*, 1902, **35**, 2700—2703).—In reply to E. Fischer (this vol., i, 428), it is shown that betaine aurichloride occurs in two modifications. When crystallised from very dilute hydrochloric acid, it is obtained in octahedra which melt and decompose at 200—209°, and when recrystallised from hydrochloric acid are converted into the rhombic modification melting at 248—250° described by Fischer (*loc. cit.*).

A third modification containing water of crystallisation is apparently obtained when the aurichloride is crystallised from water.

R. H. P.

The Action of Esters of Organic Acids on Tertiary Bases. By RICHARD WILLSTÄTTER and WALTER KAHN (*Ber.*, 1902, **35**, 2757—2761).—Tetramethylammonium benzoate (Lawson and Collie, Trans., 1888, **53**, 631) is obtained when methyl benzoate is warmed with anhydrous trimethylamine in sealed tubes for 7 hours at 160°; it melts at about 192°.

Trimethylamine and methyl acetate yield the compound

$$CH_3\cdot CO_2\cdot NMe_4,CH_3\cdot CO_2H$$

in the form of hygroscopic crystals melting at 90° and decomposing at 195°. Methyl oxalate combines with one mol. of trimethylamine only, yielding the compound $CO_2Me\cdot CO_2\cdot NMe_4$, which softens at 100°, melts at 125°, and begins to decompose at 140°.

Methyl phthalate and trimethylamine yield *methyl tetramethylammonium phthalate*, $CO_2Me\cdot C_6H_4\cdot CO_2\cdot NMe_4$, in the form of colourless plates softening at 132°, and completely melting at 150°. J. J. S.

Mechanism of the Synthesis of Leucine. By A. VILA and E. VALLÉE (*Compt. rend.*, 1902, **134**, 1594—1597. Compare this vol., i, 207).—This paper is a more detailed account of the preparation and properties of the substances obtained by Étard and Vila (*loc. cit.*) in the synthesis of leucine from active valeraldehyde, $CH_2Me\cdot CHMe\cdot CHO$. Valeraldehyde-ammonia, $C_5H_{10}O,NH_3$, is obtained as an oil by exposing the hydrate over baryta; it absorbs water from the air, re-forming crystals of the hydrate. The nitrile, prepared from the ammonia derivative, crystallises in long needles melting at 58°; its mol. weight (in benzene) corresponds with that required for the formula $C_{12}H_{21}N_3$ (compare *loc. cit.*); on passing hydrogen chloride into its ethereal solution, a crystalline *hydrochloride* is formed melting at 86°. K. J. P. O.

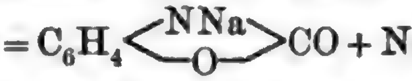
Structurally Isomeric Mercury Cyanurates. By ARTHUR HANTZSCH (*Ber.*, 1902, **35**, 2717—2723).—*Mercuric cyanurate*, $(C_3N_3)_2(Ohg)_3,2H_2O$, obtained when a solution of trisodium cyanurate or a solution of cyanuric acid with three mols. of sodium hydroxide is precipitated at 0° with a solution of mercuric acetate or chloride, is decomposed by alkalis with the separation of mercuric oxide.

Mercuric iso*cyanurate*, $(CO)_3(Nhg)_3,2H_2O$, obtained in a similar manner at 100°, is indifferent to alkalis and can be boiled with sodium hydroxide without losing its white colour. R. H. P.

Thiocyano-compounds of Cadmium. By HERMANN GROSSMANN (*Ber.*, 1902, **35**, 2665—2669).—Cadmium thiocyanate, $Cd(SCN)_2$, can be prepared from barium thiocyanate and cadmium sulphate, and forms crystalline crusts. A *compound*, $Cd(SCN)_2,NH_3$, is formed when cadmium hydroxide is boiled with ammonium thiocyanate; it forms large, monoclinic crystals, and is decomposed by water; addition of ammonia to its aqueous solution converts it into the *compound* $Cd(SCN)_2,2NH_3$. In the mother liquor from the latter, an *ammonium cadmiothiocyanate*, $(NH_4)_2Cd(SCN)_4,2H_2O$, is contained; it crystallises in monoclinic plates which melt in their water of crystallisation at 25°. The *potassium* salt, prepared from the ammonium salt, crystallises in octahedra, the *rubidium* salt in six-sided leaflets. *Rubidium thiocyanate*, RbSCN, crystallises in long, prismatic needles. The *sodium* salt, $NaCd(SCN)_3,3H_2O$, prepared from a solution of cadmium thiocyanate and sodium thiocyanate, forms hexagonal plates. The *barium cadmium* double salt, $4Ba(SCN)_2,Cd(SCN)_2,10H_2O$, crystallises in large, four-sided plates. K. J. P. O.

Hofmann's Reaction. Conversion of Amides into Amines.

By CARL GRAEBE and SERGE ROSTOVZEFF (*Ber.*, 1902, **35**, 2747—2752).—Comparative experiments have proved that sodium hypochlorite is a more valuable reagent than the hypobromite in Hofmann's reaction, mainly on account of the fact that it is more stable. The experiments were carried out with phthalimide and its chloro-derivatives and also with *o*-benzylbenzamide. The Hofmann reaction is probably to be represented as taking place in the following stages: 1, $X\cdot CO\cdot NH_2 + NaClO = X\cdot CO\cdot NNaCl + H_2O$; 2, $X\cdot CO\cdot NNaCl \rightarrow X\cdot NNa\cdot COCl$; 3*a*, when excess of alkali is present, $X\cdot NNa\cdot COCl + 2NaOH = X\cdot NH_2 + NaCl + Na_2CO_3$ or 3*b*, when excess of alkali is not present, $2X\cdot NNa\cdot COCl + H_2O = (X\cdot NH)_2CO + 2NaCl + CO_2$. As proof of this, the authors find that a theoretical yield of diphenylcarbamide is obtained when benzoylchloroamide (1 mol.) is left in contact with sodium hydroxide (1 mol.).

The third stage of the reaction can proceed in a different manner when the formation of a stable ring is possible, 3*c*,  $ONa\cdot C_6H_4\cdot NNa\cdot COCl = C_6H_4{<}{\overset{NNa}{\underset{O}{}}}{>}CO + NaCl$. This reaction is typified in the case of salicylamide, which, when treated with sodium hypochlorite in the presence of excess of alkali, yields oxycarbanil. The amide of methylsalicylic acid under similar conditions yields anisidine. J. J. S.

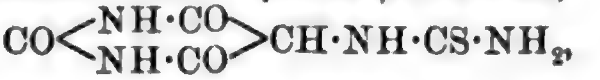
Attempts to prepare Thionic and Dithionic Acids in the Fatty Series.

By C. V. JÖRGENSEN (*J. pr. Chem.*, 1902, [ii], **66**, 28—46).—The nitriles, when treated with sodium hydrogen sulphide in aqueous or dilute alcoholic solution, yield only the sodium salts of the corresponding fatty acids, and when treated with an alcoholic solution of sodium hydrogen sulphide, yield thioamides. The salt obtained by Dupré (Abstr., 1878, 568) in an analogous manner in the presence of an excess of hydrogen sulphide is sodium thiosulphate.

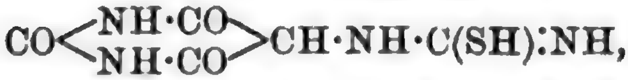
Thioacetamide, when treated with sodium ethoxide, yields sodium sulphide, alcohol, acetonitrile, mercaptan, sodium thiosulphate and acetate, and ammonia. Methylthioacetanilide is hydrolysed by dilute alcoholic sodium hydroxide, yielding methylaniline and sodium thiosulphate and sulphide, but is not affected by an alcoholic solution of sodium hydrogen sulphide. Ethyl*iso*thioacetanilide reacts with carbon disulphide at 180—200°, yielding ethyl mercaptan, aniline, and an undetermined *compound*, which crystallises from alcohol and melts at 148°.

Carbon disulphide reacts with sodium zinc methyl at 110°, forming *iso*propyl mercaptan and several inorganic salts. Attempts to prepare thioacetyl chloride (i) by action of phosphorus pentasulphide on acetyl chloride, and (ii) by heating the salt, $CSMe\cdot NH_2,HCl$, were failures. The action of acetyl chloride on thioacetamide yielded a yellow, crystalline mass, which is probably an additive compound of both reagents. R. H. P.

Conversion of *iso*Uric Acid into Uric Acid and Thioxanthine. By Emil Fischer and Hermann Tüllner (*Ber.*, 1902, **35**, 2563—2571).—*iso*Uric acid is converted completely into uric acid by heating with 20 per cent. hydrochloric acid. *γ-Thio ψ-uric acid*,



$$CO<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CH\cdot NH\cdot CS\cdot NH_2,$$



or $CO<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CH\cdot NH\cdot C(SH)\colon NH$, is readily prepared by the action of ammonium sulphide on *iso*uric acid and can be isolated by precipitating the barium salt with sulphuric acid and evaporating the filtrate under 20 mm. pressure; it forms minute, colourless needles, is exceedingly soluble in water, gradually decomposes in aqueous solution with formation of thioxanthine and sulphur, and decomposes when heated with liberation of gas. The *ammonium* salt crystallises in colourless, glistening needles or thin prisms, becomes dark and decomposes with liberation of gas at about 255°, and, unlike the *iso*urate, does not become red when the aqueous solution is exposed to air. The *sodium* salt forms a paste of minute needles and has the composition

$$C_5H_5O_3N_4SNa,\tfrac{1}{2}H_2O,$$

although the water of crystallisation could not be directly determined. The *potassium* salt also forms very minute needles. The *barium* salt, $(C_5H_5O_3N_4S)_2Ba,3H_2O$, crystallises from hot water in colourless prisms and begins to decompose at 109° before the water of crystallisation is lost. The *platinum* compound has the formula,

$$(C_5H_5O_3N_4S)_2Pt,H_2O,$$

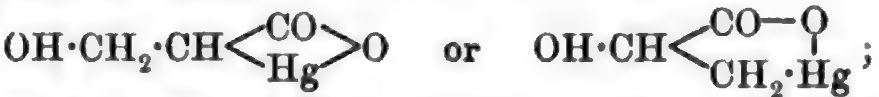
or perhaps $(C_5H_4O_3N_4S)_2Pt$, and forms yellow, glistening crystals.

The conversion of γ-thio-ψ-uric acid into thioxanthine is readily brought about by heating the ammonium salt with 20 per cent. hydrochloric acid on a water-bath for half-an-hour. T. M. L.

Solubility of Prussian Blue under certain Conditions. By Ch. Coffignier (*Bull. Soc. Chim.*, 1902, [iii], **27**, 696—699).—When treated in the cold with hydrochloric acid, Prussian blue dissolves to a certain extent, furnishing a green solution; on heating, more of the blue passes into solution. If the solution contains more than 2 grams of Prussian blue per litre, a deposit of hydroferrocyanic acid separates on standing. On employing mixtures of equal volumes of hydrochloric acid and alcohols of the fatty series, a much larger quantity of

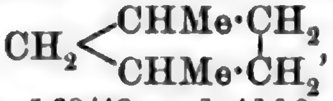
Prussian blue dissolves, the solutions being of a faint yellow to dark brown or reddish colour. In the case of hydrochloric acid and ethyl alcohol, the solutions containing 10 grams or more of Prussian blue per litre yield a deposit when kept, but with mixtures of hydrochloric acid and propyl or *iso*butyl alcohol, stable solutions can be obtained containing as much as 20 grams per litre. In the case of hydrochloric acid and amyl alcohol, as much as 40 grams per litre can be dissolved, but when the quantity exceeds 20 grams per litre, two liquid layers are produced. In all cases, the addition of a small quantity of water suffices to produce a blue precipitate. A. F.

Organic Mercury Compounds. By Einar Biilmann (*Ber.*, 1902, **35**, 2571—2588).—Mercury acrylate is soluble both in acids and alkalis and is formulated as



$$\mathrm{OH{\cdot}CH_2{\cdot}CH}\left<\begin{matrix}\mathrm{CO}\\ \mathrm{Hg}\end{matrix}\right>\mathrm{O} \quad \text{or} \quad \mathrm{OH{\cdot}CH}\left<\begin{matrix}\mathrm{CO-O}\\ \mathrm{CH_2{\cdot}Hg}\end{matrix}\right. ;$$

it is also soluble in sodium chloride, perhaps with formation of $\mathrm{OH{\cdot}CH_2{\cdot}CH(HgCl){\cdot}CO_2Na}$, whilst potassium iodide gives mercuric iodide and potassium acrylate. Compounds of similar type are formed from crotonic acid, maleic acid, itaconic acid, and citraconic acid, whilst fumaric acid and mesaconic acid yield only normal mercury salts. Malonic acid and ethyl malonate yield compounds in which the hydrogen of the methylene group is replaced by mercury. Experiments with acetone, ethyl acetoacetate, and acetylacetone are also described. T. M. L.

Optically Active Saturated Cyclic Hydrocarbons (Active Naphthenes). By Nicolai Zelinsky (*Ber.*, 1902, **35**, 2677—2682).—*d*-1 : 3-Dimethyl-3-*cyclo*pentanol readily yields the corresponding *iodide*, which is lævorotatory and has a_D − 2°39′ ($l = 0{\cdot}25$ dcm.). This substance is converted by reduction with zinc dust and acetic acid into active 1 : 3-*dimethyl*cyclo*pentane*,  $\mathrm{CH_2}\left<\begin{matrix}\mathrm{CHMe{\cdot}CH_2}\\ \mathrm{CHMe{\cdot}CH_2}\end{matrix}\right.$, which boils at 90·5—91°, has a sp. gr. 0·7497 at 16°/4°, n 1·4110 at 18°, and $[a]_D$ +1·78°. The stereoisomerism is due to the *cis-trans*-position of the methyl group. Apart from optical activity, this compound agrees in physical properties with the inactive hydrocarbon prepared from dimethyladipic acid.

Active 1-*methyl*-3-*ethyl*cyclo*pentane*, C_8H_{16}, is prepared from methylethyl-3-*cyclo*pentanol, and boils at 120·5—121°; it has a sp. gr. 0·7669 at 16°/4°, n 1·4214 at 16°, and $[a]_D$ +4·34°. In this case, two pairs of stereoisomerides are possible, the *cis-cis*- and the *cis-trans*-forms.

Active 1 : 3-*dimethyl*cyclo*hexane*, C_8H_{16}, boils at 119·5—120°, has a sp. gr. 0·7661 at 26°/4°, n 1·4218 at 26°, and $[a]_D$ about +0·65°. This hydrocarbon is derived from a crystalline 1 : 3-*dimethyl*cyclo*hexanol*, obtained by the fractionation of the liquid compound previously described (Abstr., 1901, i, 660), which crystallises from light petroleum in very soft, fascicular aggregates of needles melting at 71—72°. It has $[a]_D$ +7°15′ and is stereoisomeric with the liquid alcohol previously obtained. The corresponding *iodide* boils at 83·5—84·5° under 16 mm. pressure.

3-*Bromo*-1-*methyl*-3-*ethyl*cyclo*hexane*, prepared from the corresponding optically active alcohol, boils at 90—92° under 20 mm. pressure, has a sp. gr. 1·1828 at 16°/4°, and a_D + 1°2′ ($l = 0·25$ cm.).

Active 1-*methyl*-3-*ethyl*cyclo*hexane* boils at 148—149° (corr.), has a sp. gr. 0·7896 at 17°/4°, n 1·4353 at 17°, and $[a]_D$ − 2·9°.

It is noteworthy that the saturated cyclic hydrocarbons are much less optically active than the unsaturated hydrocarbons of the same class. A. H.

Migration of the Phenyl Group in Styrene and its Derivatives. By Marc Tiffeneau (*Compt. rend.*, 1902, **134**, 1505—1507).—When subjected to the action of silver nitrate, the iodohydrin of diphenylethylene, $Ph_2C{:}CH_2$, gives deoxybenzoin, $Ph·CO·CH_2Ph$, the formation of which can only be explained by a migration of one of the phenyl groups.

Styrene iodohydrin, when treated with sulphuric acid, gives phenylacetaldehyde, $CPh{:}CH \rightarrow CH_2Ph·CHO$, and since under the same conditions phenylmethyl glycol, $OH·CPhMe·CH_2·OH$, gives hydratropic aldehyde, $CHMePh·CHO$, it is concluded that in the action with sulphuric acid it is a hydrogen atom and not the phenyl group which migrates.

With silver nitrate, phenylpropylene iodohydrin gives phenylacetone, proving that the phenyl group migrates.

When treated with silver nitrate, the iodohydrin of phenyl*iso*butylene, $Me_2C{:}CHPh$, gives dimethylphenylacetaldehyde,

$$CMe_2Ph·CHO,$$

and in this case it is quite certain that it is the phenyl group which changes its place.

The migration of the phenyl group gives an explanation of the different behaviour of these ethylene derivatives towards mercuric oxide and silver nitrate. In all cases, reaction takes place with the latter, but only when the phenyl group is substituted (by one or more methoxy-groups in *iso*safrole, anethole, and ψ-anethole) does reaction take place with mercuric oxide.

Finally, it has been proved that the tolyl group migrates more readily than does the phenyl radicle. Thus, the iodohydrin of *as*-phenyltolylethylene, $PhCH_2·CPh{:}CH_2$, gives phenyl *p*-xylyl ketone, $Ph·CO·CH_2·C_6H_4Me$. J. McC.

Styrenes. II. By August Klages (*Ber.*, 1902, **35**, 2633—2646. Compare this vol., i, 611).—Grignard (Abstr., 1900, i, 382) has shown that a ketone (1 mol.) such as acetophenone reacts with methyl iodide (1 mol.) and magnesium (1 atom) forming the tertiary alcohol, phenyldimethylcarbinol. If, however, 2 mols. of the alkyl iodide and 2 atoms of magnesium are used and the mixture heated for several hours, an ethylene derivative is alone obtained, in this case, β-allylbenzene. This reaction appears to be perfectly general, except when two ortho-substituents are present, as in acetylmesitylene. By means of sodium and alcohol, the ethylene derivatives can be easily reduced to the corresponding saturated hydrocarbons.

Magnesium ethiodide and acetylmesitylene yield an *additive* product, $C_6H_2Me_3\cdot CMeI\cdot O\cdot MgEt,OEt_2$, which forms a crystalline powder and reacts violently with water, re-forming acetylmesitylene.

β-Allylbenzene, $CH_2\dot{:}CPhMe$ (Tiffeneau, this vol., i, 433), is obtained when the additive compound prepared from magnesium methyl iodide and acetophenone is decomposed by water at a high temperature; unchanged acetophenone is always mixed with the hydrocarbon. It is also formed when phenyldimethylcarbinol is heated with magnesium methyl iodide (compare Tiffeneau, *loc. cit.*). The additive compound just mentioned is a lustrous, crystalline powder; when decomposed with dilute acid or ice-cold water, phenyldimethylcarbinol is alone formed; if the compound contains unchanged acetophenone, a mixture is produced which cannot be separated by distillation; the pure carbinol boils at 93—94° under 13 mm., and at 202° under the ordinary pressure, and has a sp. gr. 0·9724 at 18·5°/4°.

*β-Chloro*iso*propylbenzene*, $C_6H_5\cdot CMe_2Cl$, is prepared when hydrogen chloride is led into the carbinol cooled to 0°; it is a colourless oil which evolves hydrogen chloride when heated and is converted into methylvinylbenzene on boiling with pyridine. The corresponding *iodine* derivative is an unstable, heavy oil; if its solution in acetic acid, or a solution of the carbinol in acetic acid containing hydriodic acid, is treated with zinc dust and the product neutralised and then distilled in steam, an oil, probably *iso*propylbenzene, distils, and a *substance*, $C_{18}H_{22}$, remains, which crystallises in needles melting at 119—120°, is stable towards permanganate and does not decolorise bromine; this substance is not identical with tetramethyldiphenylethane (Wallach, Abstr., 1900, i, 229), which melts at 55—56°; it is possibly a *cyclo*butane derivative.

α-Iodoethylbenzene, $C_6H_5\cdot CHMeI$, is prepared in a similar manner from phenylmethylcarbinol, and is a heavy, unstable oil; with zinc dust, it yields dimethyldibenzyl (m. p. 126°).

On warming phenyldimethylcarbinol with syrupy phosphoric acid, it is converted into β-allylbenzene (b. p. 165—168°), and a *bimolecular* β-allylbenzene, $CPhMe\dot{:}CH\cdot CH_2\cdot CHPhMe$ (?). The latter is a viscous, odourless oil boiling at 302° and having a sp. gr. 0·9724 at 21°/4°; it reduces permanganate slowly and unites with bromine; it is not reduced to *iso*propylbenzene by sodium and alcohol.

1^1-*Metho*-1^1-*propenylbenzene* (*β-phenyl-*Δ^β*-butylene*), $CPhMe\dot{:}CHMe$, is prepared by mixing ethyl iodide, acetophenone, and magnesium in the presence of ether, heating for 5 hours after distilling off the ether, and then decomposing the crystalline mass with dilute sulphuric acid. It is an oil with a pleasant odour boiling at 191—193° and has a sp. gr. 0·9221 at 15°/4°; it forms an oily dibromide; it is oxidised by permanganate to acetophenone and reduced by sodium and alcohol to secondary butylbenzene (b. p. 172—173°).

1^1-*Metho*-1^1-*propenyl*-p-*iodobenzene* (*β*-p-*iodophenyl-*Δ^β*-butylene*),

$C_6H_4I\cdot CMe\dot{:}CHMe$,

is prepared in a similar manner from *p*-iodoacetophenone; it is an oil with a pleasant odour, boiling at 155° under 23 mm. pressure, and crystallising in colourless leaflets which melt at 45—46°; it is oxidised to *p*-iodoacetophenone and is reduced to a mixture of *p*-iodo-*sec.*butylbenzene and *sec.*butylbenzene.

1^1-*Metho*-1^1-*butenylbenzene* (*β-phenyl-Δ^β-amylene*), $CPhMe{:}CHEt$, is prepared from propyl iodide and acetophenone; the first product of the reaction is *phenylmethylpropylcarbinol*, $OH{\cdot}CPhMePr$, an oil boiling at 112—113° under 12 mm., at 116—117° under 16 mm., and at 216° under the ordinary pressure, and having a sp. gr. 0·9723 at 21·5°/4°. The *chloro*-derivative, $CClPhMe{\cdot}CH_2Et$, prepared by the action of hydrogen chloride at 0° on the carbinol, is an unstable oil, which, when boiled with pyridine, is converted into the hydrocarbon; the latter is a colourless, limpid oil, which boils at 89—90° under 16 mm. and at 199° under the ordinary pressure, and has a sp. gr. 0·8976 at 21·2°/4°; it is oxidised to acetophenone and reduced to a sec.*amylbenzene*, $C_6H_5{\cdot}C_5H_{11}$, which boils at 191°.

$1^1 : 1^4$-*Dimetho*-1^1-*pentenylbenzene* (*β-phenyl-Δ^β-*iso*heptylene*),

$CPhMe{:}CH{\cdot}CH_2Pr^\beta$,

obtained from *iso*amyl iodide and acetophenone, is an oily liquid boiling at 121° under 20 mm. pressure and having a sp. gr. 0·8814 at 15°/4°; it is oxidised to acetophenone and valeric acid and reduced to an iso*heptylbenzene*, $CHPhMe{\cdot}CH_2{\cdot}CH_2Pr^\beta$, which boils at 223° and has a sp. gr. 0·8696 at 15°/4°.

6^1-*Metho*-6^1-*propenyl*-1 : 3 : 4-*trimethylbenzene* (*β-ψ-cumyl-Δ^β-butylene*), $C_6H_2Me_3{\cdot}CMe{:}CHMe$, prepared from aceto-ψ-cumene and ethyl iodide, is a colourless oil boiling at 234—236° and having a sp. gr. 0·8992 at 15°/4°; it is not easily attacked by permanganate. K. J. P. O.

Synthesis of Arylated Ethylenes. By August Klages (*Ber.*, 1902, **35**, 2646—2649. Compare Abstr., 1899, i, 598).—Diphenylmethylcarbinol, $CPh_2Me{\cdot}OH$, is easily prepared by treating a benzene solution of benzophenone with magnesium and a solution of methyl iodide in ether, and acting on the crystalline mass which is thus formed with ice-cold dilute sulphuric acid; it crystallises in prisms melting at 81°. If the mixture just mentioned is heated for some time at 100°, *as*-diphenylethylene is also produced; the unsaturated hydrocarbon can be obtained from the carbinol by first converting it into the chloride by means of hydrogen chloride and then boiling the latter with pyridine. When *as*-diphenylethylene is reduced with sodium and alcohol, *as*-diphenylethane is formed as a colourless oil boiling at 148° under 22 mm. pressure and having a sp. gr. 0·9877 at 25°/4°; prepared by this method, the hydrocarbon does not exhibit a blue fluorescence. *s*-Diphenylethylene is also very easily reducible to the corresponding ethane, dibenzyl, by the same reagent.

aa-Diphenylpropylene, $CPh_2{:}CHMe$, prepared in a similar manner from benzophenone and ethyl iodide, forms colourless crystals melting at 52° and boiling at 169—170° under 28 mm. pressure; it is reduced by sodium and alcohol to *diphenylpropane*, $CPh_2{\cdot}CH_2Me$, which is a colourless oil boiling at 153—154° at 20 mm. pressure and has a sp. gr. 0·9751 at 23°/4°.

aβ-Diphenylpropylene, $CHPh{:}CPhMe$, is prepared from deoxybenzoin and methyl iodide in the presence of magnesium; it crystallises in plates or leaflets melting at 82—83° and boiling at 183° under 26 mm. pressure. When oxidised by permanganate, only benzoic acid was formed; with chromic acid, on the other hand, acetophenone and benzoic acid are produced. On reduction, the corresponding diphenylpropane is obtained as an oil which boils at 166—167° under 28 mm. pressure and has a sp. gr. 0·9824 at 23°/4°. K. J. P. O.

Phenylbutadiene. By AUGUST KLAGES (*Ber.*, 1902, **35**, 2649—2652).—*Methylstyrylcarbinol*, CHPh:CH·CHMe·OH, is prepared from cinnamaldehyde, methyl iodide, and magnesium; the crystalline double compound first formed is decomposed by water; the carbinol is a viscous oil boiling at 144° under 21 mm. pressure, and has a sp. gr. 1·0134 at 22°/4°. The *phenylurethane*, $C_{17}H_{17}O_2N$, obtained from the carbinol and phenylcarbimide, crystallises in needles melting at 94—95°. The *chloride*, ChPh:CH·CHClMe, prepared by the action of hydrogen chloride on an ethereal solution of the carbinol, is a pale yellow, unstable oil.

a-Phenylbutadiene, $CHPh:CH·CH:CH_2$, obtained by boiling the chloride with pyridine, is a colourless oil boiling at 94—96° under 18 mm. pressure; it is oxidised by the air to a colourless balsam, and polymerises on attempting to distil it under the ordinary pressure. The compound obtained by Doebner (this vol., i, 598) by the dry distillation of cinnamenylacrylic acid with barium hydroxide is, therefore, not phenylbutadiene, whereas the compound prepared by Liebermann and Riiber (Abstr., 1900, i, 648) by distilling *allo*cinnamylideneacetic acid in a vacuum is this hydrocarbon.

The *tetrabromide* of phenylbutadiene, $CHPhBr·CHBr·CHBr·CH_2Br$, forms colourless leaflets melting at 146°. On reducing the hydrocarbon with sodium and alcohol, *a-phenyl-Δ^{β}-butylene*, $CH_2Ph·CH:CHMe$, is obtained; its *dibromide* is an oil.

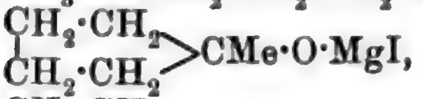
a-Phenyl-γ-methyl-$\Delta^{a\gamma}$-butadiene, $CHPh:CH·CMe:CH_2$, was prepared by treating benzylideneacetone with magnesium and methyl iodide in ethereal solution, and then adding dilute sulphuric acid to the clear liquid; in this case, the hydrocarbon was obtained directly without the intermediate formation of the carbinol. It is an oil boiling at 124° under 32 mm. pressure, and has a sp. gr. 0·9423 at 23°/4°; on reduction, a dihydro-product, probably *amenylbenzene*, $CH_2Ph·CH_2·CMe:CH_2$, is formed; it is an oil boiling at 205° and forms a *dibromide*, $C_{11}H_{14}Br_2$, which crystallises in leaflets melting at 65—66°.

a-Phenyl-γ-methyl-$\Delta^{a\gamma}$-pentadiene, CHPh:CH·CMe:CHMe, prepared from benzylideneacetone and ethyl iodide by a similar method, is a colourless oil with an odour of turpentine; it boils at 132—133° under 21 mm. pressure and has a sp. gr. 0·9523 at 23°/4°; it is oxidised by the air. K. J. P. O.

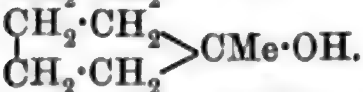
***allo*Phenylbutadiene.** By CARL LIEBERMANN and C. N. RIIBER (*Ber.*, 1902, **35**, 2696—2698).—When cinnamylidenemalonic acid is heated at 180° with quinoline, the *allo*cinnamylideneacetic acid, which is first formed (see Abstr., 1895, i, 470), is converted into allo*phenylbutadiene*, $CHPh:CH·CH:CH_2$; this melts at 4·5°, boils at 95° under 20 mm. pressure, and has a sp. gr. 0·9286 at 20°/4°, and an odour like that of styrene. When heated at 250°, it polymerises to bis*diphenylbutadiene*, $C_{20}H_{20}$, which is a thick, viscous oil boiling at 221° under 17 mm. pressure, and has a sp. gr. 1·0325 at 28°/4°, and n_D 1·6016 at 20°.

*allo*Phenylbutadiene differs from the phenylbutadiene described by Doebner (this vol., i, 598) as it combines with 2 mols. of bromine (compare Klages, preceding abstract). R. H. P.

Ring Formation by means of Magnesium Organic Compounds. A complete Synthesis of Methyl*cyclo*pentane. By Nicolai Zelinsky and A. Moser (*Ber.*, 1902, 35, 2684—2686).—*δ-Acetylbutyl iodide*, $CH_2Ac\cdot CH_2\cdot CH_2\cdot CH_2I$, prepared from the corresponding alcohol, forms an almost colourless liquid which boils at 117° under 14 mm. pressure and has a sp. gr. 1·5838 at 23°/4°. It readily reacts with metallic magnesium, yielding an additive product which, when decomposed by dilute acetic acid, yields 1-methyl-1-*cyclo*pentanol. It seems probable that the additive compound $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot MgI$ passes into the form



$\left|\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\right. \!>CMe\cdot O\cdot MgI$, and that this yields with water the alcohol



$\left|\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\right. \!>CMe\cdot OH$.

The reaction does not occur with metallic zinc. The alcohol can readily be converted into the iodide, and this, by reduction with zinc dust in presence of acetic acid saturated with hydriodic acid, into the corresponding hydrocarbon, methyl*cyclo*pentane, boiling at 72—72·2° (corr.). A. H.

Influence of Alkyl Groups on the Activity of Halogenised Benzenes. By August Klages and W. Storp (*J. pr. Chem.*, 1902, [ii], 65, 564—578. Compare Abstr., 1901, i, 387).—The elimination of halogen from the benzene nucleus is favoured by the presence of methyl in the ortho-, diortho-, or ortho-para-positions, but made more difficult by the presence of a homologue of methyl. The elimination of iodine by treatment with red phosphorus and hydriodic acid is effected with *p*-iodotoluene in two hours at 182°; with *p*-iodoethylbenzene in five hours at 218°; *p*-iodo*iso*butylbenzene and *p*-iodo-*tert.*-butylbenzene are unchanged in five hours at 218°; and iodocetylbenzene does not undergo the reaction at 230°.

The introduction of iodine into the benzene nucleus is similarly effected. When boiled with iodine and iodic acid in glacial acetic acid solution, benzene is not attacked, toluene reacts slowly, ethylbenzene and *iso*butylbenzene are easily iodinated, but cetylbenzene reacts very slowly. Mesitylene, *s*-dimethylethylbenzene, and *s*-triethylbenzene react easily, but *s*-triphenylbenzene is only slightly attacked after three hours' boiling.

The following new compounds are described:

p-*Iodoethylbenzene* is a colourless oil, boils at 112° under 20 mm. pressure, has a sp. gr. 1·65 at 14°, and forms an *iododichloride*, $C_8H_9ICl_2$, as a yellow, crystalline mass melting at 90°. p-*Iodoisobutylbenzene* is a colourless oil, boils at 120—121° under 11 mm. pressure, and has a sp. gr. 1·44 at 11°.

p-*Iodocetylbenzene* crystallises in colourless leaflets, melts at 38°, and forms an *iododichloride*, $C_{22}H_{37}ICl_2$, as a yellowish-green, crystalline mass which melts and decomposes at 86°. 2-*Iodocymene*, prepared from 2-cymidine, is a colourless oil, boils at 139° under 23 mm. pressure, and has a sp. gr. 1·46 at 14°. The *iododichloride*, $C_{10}H_{13}ICl_2$, forms yellow crystals and melts and decomposes at 92·5°. 3-*Iodocymene*, formed by the action of iodine and iodic acid on cymene, is a colourless oil, boils at 122—124° under 13 mm. pressure, and has a sp. gr. 1·52 at 13°. The *iododichloride* melts at 87°, and is easily soluble in chloroform, but more sparingly so in carbon tetrachloride. 2-*Iodo*-1-*methyl*-3-tert.-*butyl benzene*, prepared from the amine, is a colourless oil, boils at 132—133° under 13 mm. pressure, and has a sp. gr. 1·46 at 13°.

Iododimethylethylbenzene [$I : Me_2 : Et = 2 : 1 : 3 : 5$], formed from *s*-dimethylethylbenzene, is a colourless oil, boils at 142—144° under 22 mm. pressure, and has a sp. gr. 1·54 at 13°. *Iodocetylmesitylene* melts at 44°.
G. Y.

Reduction of Aromatic Nitro-compounds with Tin and Hydrochloric Acid. By JOHANNES PINNOW (*J. pr. Chem.*, 1902, [ii], **65**, 579—585. Compare Abstr., 1901, i, 485).—Experimental proof is given that the addition of graphite accelerates the reduction of nitro-compounds with tin and hydrochloric acid. As in the reduction of nitrodimethyltoluidine under these conditions, 1 : 5-dimethylbenziminazole is not formed, the nitroso-compound cannot be an intermediate stage in the process (compare Haber, Abstr., 1900, i, 592). 1 : 5-Dimethylbenziminazole is formed in small quantity when the reduction is electrolytic, the yield being greater with a carbon than with a platinum cathode; when the reduction is retarded by introduction of a resistance, the proportion of the benziminazole formed remains unchanged, but the proportion of chloro-compounds is increased.
G. Y.

Combination of Alcohol with Nitro-derivatives of Styrene. By BERNHARD FLÜRSCHEIM (*J. pr. Chem.*, 1902, [ii], **66**, 16—27).—When ω-bromostyrene is treated with cold fuming nitric acid, two dinitrobromostyrenes are obtained in addition to *p*-nitrobenzoic acid. α-p-*Nitrophenyl*-β-*bromonitroethylene* separates from alcohol in yellow crystals, melts at 135—136°, combines only slowly with bromine, and, when boiled with water, yields *p*-nitrobenzaldehyde, nitrobromomethane, nitric acid, and hydrogen bromide; when boiled with ethyl alcohol, it yields α-p-*nitrophenyl*-α-*ethoxy*-β-*nitrobromoethane*, which forms colourless crystals, melts at 95—96°, dissolves in caustic alkalis giving yellow solutions, which are decolorised by bromine, giving α-p-*nitrophenyl*-α-*ethoxy*-β-*nitrodibromoethane* melting at 145·5°. α-o-*Nitrophenyl*-β-*bromonitroethylene* crystallises from acetic acid, melts at 88°, and is decomposed by water into *o*-nitrobenzaldehyde and bromonitromethane; it is insoluble in alkalis and combines with alcohol far less readily than the *p*-derivative forming the ethoxy-compound, which melts at about 60°, and with bromine yields the α-o-*nitrophenyl*-α-*ethoxy*-β-*nitrodibromoethane* melting at 70·5°. ω-Nitrostyrene, *p*-ω-dinitrostyrene, and ω-bromostyrene do not combine with boiling ethyl alcohol.

The paper concludes with a discussion of the conditions necessary for the addition of ethyl alcohol to an ethylene derivative, and of the formulæ of primary and secondary nitro-compounds. R. H. P.

9-Aminophenanthrene. By Robert Pschorr and J. Schröter (*Ber.*, 1902, **35**, 2726—2729. Compare Schmidt and Strobel, Abstr., 1901, i, 464).—*Ethyl phenanthrene-9-carboxylate* crystallises in needles or flat plates, melts at 61°, and is readily soluble in the usual organic solvents. The *hydrazide*, $C_{14}H_9 \cdot CO \cdot NH \cdot NH_2$, crystallises from hot water or benzene in colourless needles melting at 228° and readily soluble in glacial acetic acid. On treatment with sodium nitrite solution, it is converted into the *azoimide*, $C_{14}H_9 \cdot CO \cdot N_3$, melting at 94°, and this, when warmed with alcohol, yields 9-phenanthrylurethane.

9-Hydroxyphenanthrene is obtained when the urethane is hydrolysed with concentrated hydrochloric acid and 9-aminophenanthrene when the urethane is heated with concentrated ammonia at 180° for two hours. J. J. S.

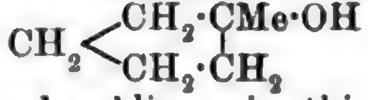
9-Amino-10-hydroxyphenanthrene, Morphigenin, and 9 : 10-Diaminophenanthrene. By Robert Pschorr [with J. Schröter] (*Ber.*, 1902, **35**, 2729—2740).—Vahlen's morphigenin chloride, 9-amino-10-hydroxyphenanthrene hydrochloride (*Arch. exp. Path. Pharm.*, 1902, **47**, 368), may be obtained by the reduction of phenanthraquinoneimide or of phenanthraquinone monoxime with stannous chloride and hydrochloric acid. When warmed with water or dilute acids, it is converted into phenanthraquinol; nitrous or nitric acid yields phenanthraquinone. The free base may be obtained by the action of alkali sulphite, acetate, or carbonate on the hydrochloride in the absence of air; it forms brownish needles, begins to sinter at 150°, and is completely melted at 417°. It dissolves in alkali without undergoing decomposition if air is absent. When the alkaline solution is warmed in an atmosphere of hydrogen, the products are ammonia and 9 : 10-dihydroxyphenanthrene, the *acetyl* derivative of which melts at 202°. In the presence of air, the products are the corresponding quinone and quinhydrone.

9-*Acetylamino*-10-*hydroxyphenanthrene* crystallises in colourless, flat needles melting at 223—224° (corr.), and on further treatment with acetic anhydride yields 9-*acetylamino*-10-*acetoxyphenanthrene*, which crystallises from acetic acid in six-sided prisms melting at 242° (corr.). Benzoyl chloride converts the base into *anhydrobenzoyl*-10-*hydroxy*-9-*aminophenanthrene*, $C_{21}H_{13}ON$, which crystallises in glistening needles melting at 205° (corr.).

10-*Hydroxy*-9-*phenanthrylphenylcarbamide*, $C_{21}H_{16}O_2N_2$, obtained by the action of phenylcarbimide on the base, crystallises in small needles melting at 241° (corr.).

9 : 10-*Diaminophenanthrene*, obtained by the reduction of phenanthraquinonedioxime with stannous chloride and concentrated hydrochloric acid, forms yellowish plates melting at 160—166° in the crude state. Its *diacetyl* derivative crystallises in six-sided plates melting and decomposing at 330° (corr.). The free base readily loses ammonia and yields diphenanthryleneazotide (Japp, Trans., 1886, **49**, 843).

J. J. S.

Synthesis of 1-Methyl-1-*cyclo*pentanol. By Nicolai Zelinsky and S. Namjetkin (*Ber.*, 1902, **35**, 2683).—*cyclo*Pentanone, prepared from adipic acid, yields a complex product with magnesium and methyl iodide in presence of ether, and this is decomposed by water with formation of 1-*methyl*-1-cyclo*pentanol*,  $CH_2<\begin{matrix}CH_2\cdot CMe\cdot OH\\ \vert\\ CH_2\cdot CH_2\end{matrix}$, which boils at 135° under 737 mm. pressure and sublimes in thin needles melting at 35—37°. A. H.

A New Di-iodophenol. By P. Brenans (*Compt. rend.*, 1902, **135**, 177—179. Compare Abstr., 1901, i, 322, 643; and this vol., i, 280). —4-*Iodo*-o-*nitroaniline* was prepared by the action of 1 mol. of iodine chloride on 1 mol. of *o*-nitroaniline in acetic acid solution. It is isolated by distillation in steam; it separates from hot water in orange needles and melts at 122°.

By dissolving this substance in a mixture of acetic and sulphuric acids, and, after cooling, adding sodium nitrite, then pouring in a solution of potassium iodide, 3 : 6-*di-iodonitrobenzene* is formed; this crystallises from hot water in slender, yellow needles, melts at 109—110°, and is soluble in alcohol, ether, chloroform, or benzene.

When this nitro-compound is reduced in acid solution with stannous chloride, 3 : 6-*di-iodoaniline* is obtained, which crystallises from hot water in colourless needles, has an odour recalling that of naphthalene, and melts at 88—89°. It is volatile with steam and soluble in the ordinary organic solvents. Its solutions become coloured on exposure to light.

When diazotised in presence of acetic acid and sulphuric acid and then distilled in steam, the di-iodoaniline gives colourless needles of 3 : 6-*di-iodophenol*. This crystallises from light petroleum, melts at 99°, is slightly soluble in water or ether, and readily so in alcohol, acetic acid, or benzene. Its acetate, $C_2H_3O_2\cdot C_6H_3I_2$ [1 : 3 : 6], forms elongated, colourless prisms, melts at 70°, and is very soluble in acetic acid, methyl alcohol, or benzene. J. McC.

Some Derivatives of the Thiocresols. By Ch. Rabaut (*Bull. Soc. Chim.*, 1902, [iii], **27**, 690—692).—p-*Tolyl thiocyanate*, obtained from *p*-toluidine by the Sandmeyer reaction, forms a clear yellow liquid which boils without appreciable decomposition at 240—245° under the ordinary pressure, and at 155—158° under 40—50 mm. pressure; it is insoluble in water, but soluble in alcohol, benzene, chloroform, or glacial acetic acid. It does not combine with cuprous chloride. When treated with an aqueous or alcoholic solution of potassium hydroxide, p-*tolyl disulphide*, $S_2(C_6H_4Me)_2$, is obtained in the form of white crystals melting at 45°. *p*-Tolyl thiocyanate, treated with an alcoholic solution of potassium hydrogen sulphide, yields *thio*-p-*cresol*. This gives, with lead acetate, a precipitate, $(C_6H_4Me\cdot S)_2Pb$, which, when treated with bromine, gives *p*-tolyl disulphide, and with acetyl chloride the acetate of *p*-tolyl thioacetate, $C_6H_4Me\cdot SAc$; the latter is a colourless liquid which boils without decomposition at 240—243° under 760 mm. pressure. The *benzoyl ester*, $C_6H_4Me\cdot SBz$, obtained in a similar manner, forms white needles melting at 75°.

On heating a mixture of *p*-tolyl thiocyanate and chloroacetic acid in molecular proportion, saponifying the product with sodium hydroxide, and acidifying with hydrochloric acid, p-*tolylthioglycollic acid*,

$$C_6H_4Me\cdot S\cdot CH_2\cdot CO_2H,$$

is obtained in white crystals melting at 90°. It is very sparingly soluble in cold water, fairly so in boiling water, and very soluble in the usual solvents and in acetic acid. It can be synthesised by heating *p*-thiocresol with chloroacetic acid, and on oxidation with chromic acid yields *p*-sulphobenzoic acid. The corresponding *o-tolylthioglycollic acid*, melting at 106°, can be obtained by the action of chloroacetic acid on *o*-tolyl thiocyanate or on *o*-thiocresol. It has the same general properties as the para-compound. A. F.

Esters derived from 2 : 3-Methoxynaphthol. By RUD. ENGELHARDT (*J. pr. Chem.*, 1902, [ii], **65**, 536).—2 : 3-*Methoxynaphthol* melts at 109°. It forms a *benzoate*, which crystallises from alcohol in white leaflets and melts at 133°, a *salicylate* which crystallises in delicate needles and melts at 138°, a *valerate* which crystallises in white, soft leaflets and melts at 76°, an *acetate* which crystallises from glacial acetic acid in needles and melts at 117°, and a *phosphate* which melts above 275°. The action of phosgene on 2 : 3-methoxynaphthol in aqueous solution leads to the formation of two *substances*, the one of which melts at 82°, and is easily soluble in alcohol, the other melts at 186°, and is sparingly soluble in alcohol, but easily so in hot benzene or chloroform; on hydrolysis, both give the 2 : 3-methoxynaphthol. G. Y.

Action of Iodine on Catechol in Pyridine Solution. By GIOVANNI ORTOLEVA (*Gazzetta*, 1902, i, **32**, 447—452).—To explain the action of iodine on quinol in pyridine solution, the author and di Stefano (this vol., i, 54) found it necessary to assume that the quinol is first converted into quinone by the oxidising action of the iodine. This assumption is now confirmed by the author's observation that resorcinol is not acted on by iodine in pyridine solution, whilst catechol, which forms *o*-benzoquinone on oxidation, gives a compound similar to that yielded by quinol.

The additive *compound* of *o*-benzoquinone and pyridine hydriodide, $C_6H_4O_2,C_5H_5N,HI$, crystallises from dilute alcohol in short, yellow needles melting at 243—245°, and from water in yellow scales, which contain $1H_2O$ and darken at 250°, but are still unfused at 263°. The *acetyl* derivative, $C_{11}H_9O_2NIAc$, is deposited from water or alcohol in yellow plates which melt at 205—207° and are soluble in alkalis, giving a blood-red solution. T. H. P.

A Methylcyclohexanose. By NICOLAI ZELINSKY and M. ROSCHDESTWENSKY (*Ber.*, 1902, **35**, 2695—2696).—1-Methyl-3-*cyclo*hexanone is converted by bromine into a *bromo*-compound, $C_7H_{11}OBr$, which boils at 106—107° under 13 mm. pressure, melts at 83—85°, and has $[\alpha]_D$ −47·9°. A liquid product, which boils at a somewhat lower temperature and attacks the eyes violently, is also formed. The solid bromo-compound is converted by concentrated aqueous potash into a keto-alcohol, *methyl*cyclo*hexanose*, $C_7H_{12}O_2$, the exact constitution of which has not been decided. This substance boils at 85—86° under 12 mm. pressure, has a sp. gr. 1·0399 at 19°/4°, *n* 1·4657 at 19°, and $[\alpha]_D$ 21·6°. It reduces Fehling's solution and silver nitrate in the cold, and yields a characteristic reddish-violet coloration with ferric chloride. This substance is of simpler constitution than the cyclic ketotriose of Harries (this vol., i, 378). A. H.

Characterisation of Pseudoacids by the Ammonia Reaction.

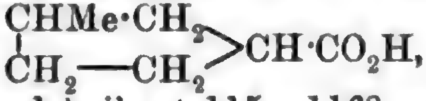
By ARTHUR HANTZSCH and E. DOLLFUS (*Ber.*, 1902, 35, 2724—2725. See this vol., i, 223).—A constant error in the calculations is noted, but it does not alter the conclusions reached in the earlier paper. R. H. P.

A Direct Synthesis of Hexahydroaromatic Acids and Polymethylenecarboxylic Acids in General.

By NICOLAI ZELINSKY (*Ber.*, 1902, 35, 2687—2692).—The iodine and bromine derivatives of *cyclo*hexane and its homologues react with metallic magnesium to form organometallic compounds which, with carbon dioxide, yield the magnesium salts of the corresponding carboxylic acids (compare Grignard, Abstr., 1901, i, 679).

By this reaction, iodo*cyclo*hexane is converted into *cyclo*hexanecarboxylic acid (hexahydrobenzoic acid); and 3-iodo-1-methyl*cyclo*hexane yields 1-methyl*cyclo*hexane-3-carboxylic acid (hexahydro-*m*-toluic acid), which boils at 134° under 15 mm. pressure.

1 : 3-*Dimethyl*-5-cyclo*hexanecarboxylic acid*, $C_6H_9Me_2\cdot CO_2H$ (hexahydro-*m*-xylylic acid), may be prepared from 5-iodo-1 : 3-dimethyl*cyclo*hexane, and boils at 139° under 15 mm. pressure. It has a sp. gr. 0·9785 at 20°/4°, *n* 1·4577 at 20°, and yields an *amide* melting at 153·5—154·5°.

1-*Methyl*cyclo*pentane-3-carboxylic acid*, 
$\begin{matrix}CHMe\cdot CH_2\\ | \\ CH_2\text{—}CH_2\end{matrix}\!>\!CH\cdot CO_2H$, is prepared from the corresponding iodide and boils at 115—116° under 15 mm. pressure. The acid has a sp. gr. 1·006 at 22°/4°, *n* 1·4480 at 22° $[\alpha]_D$ $-5·89°$. The *chloride* boils at 173—175°, and the *amide* crystallises in lustrous prisms melting at 149—150°. This acid may possibly be identical with the β-methylpentamethylenecarboxylic acid of Euler (Abstr., 1895, i, 145). Finally, *cyclo*heptanecarboxylic acid can readily be obtained in a similar manner from the *bromide* prepared from suberol, which boils at 75° under 12 mm. pressure and has a sp. gr. 1·2887 at 22°/4°, and *n* 1·4996 at 22°. A. H.

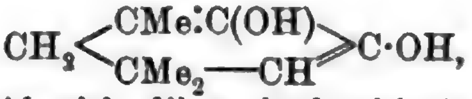
Syntheses of Benzoic Acid and Phenylacetic Acid as Lecture Experiments.

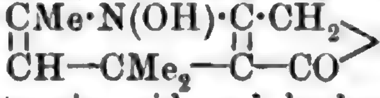
By NICOLAI ZELINSKY (*Ber.*, 1902, 35, 2692—2694).—Benzoic acid can be readily and rapidly synthesised by the action of a stream of dry carbon dioxide on an ethereal solution of magnesium phenyl iodide, which is prepared by the action of magnesium on iodobenzene in presence of dry ether. The complex magnesium compound separates as an oil which is decomposed by water with formation of magnesium benzoate. The acid is liberated by sulphuric acid, extracted with ether, and the ethereal solution washed with a few drops of sodium thiosulphate solution and evaporated, pure benzoic acid being obtained.

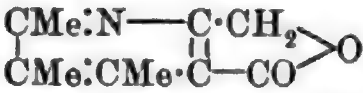
A similar reaction may be carried out with magnesium benzyl chloride, an ethereal solution of which yields, with a current of dry carbon dioxide, crystals of the formula $CH_2Ph\cdot CO_2MgCl,C_4H_{10}O$. These are decomposed by water with formation of a salt of phenylacetic acid, from which the pure acid can be readily obtained. The zinc organo-metallic compounds, such as zinc ethyl iodide, appear to undergo no reaction with carbon dioxide. A. H.

Action of Formaldehyde on Methyl Anthranilate. By HANS MEHNER (*J. pr. Chem.*, 1902, [ii], **65**, 533—536. Compare Abstr., 1901, i, 470, and Erdmann, Abstr., 1901, i, 536).—The author has confirmed his previous work and is unable to obtain Erdmann's results. G. Y.

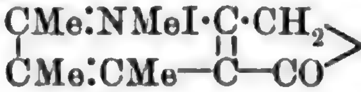
Condensation Products of Tetronic Acid. By LUDWIG WOLFF [with MAX GABLER and FRITZ HEYL] (*Annalen*, 1902, **322**, 351—391. Compare Abstr., 1901, i, 283).—The *benzoyl* derivative of ketohexyltetronic acid, prepared by treating the sodium salt with benzoyl chloride and sodium carbonate, crystallises from chloroform and light petroleum in prisms melting at 96°.

3 : 5 : 5-*Trimethyl*-$\Delta^{2:6}$-*dihydrocatechol*,  $CH_2<\begin{matrix}CMe:C(OH)\\CMe_2—CH\end{matrix}>C\cdot OH$, obtained by heating ketohexyltetronic acid with dilute hydrochloric acid for 2 hours at 120°, crystallises from dilute alcohol or ether in white, felted needles, melts at 91—92°, and sublimes without decomposition; it is neutral to litmus and gives a dark violet coloration with ferric chloride. The *dioxime*, $C_9H_{16}O_2N_2$, crystallises from dilute alcohol in needles melting at 166°; it is insoluble in sodium carbonate, but dissolves in sodium hydroxide solution or concentrated hydrochloric acid and gives a brownish-red ferric chloride coloration.

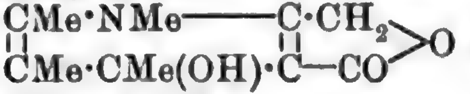
2 : 4 : 4-*Trimethyl*-N-*hydroxy*-$\Delta^{2:5}$-*dihydroquinolide*, the *pseudo-oxime* of *ketohexyltetronic acid*,  $\begin{matrix}CMe\cdot N(OH)\cdot C\cdot CH_2\\ \| \qquad\qquad \| \\ CH—CMe_2—C—CO\end{matrix}>O$, results from the interaction of ketohexyltetronic acid and hydroxylamine hydrochloride in aqueous solution; it is sparingly soluble in concentrated hydrochloric acid and the ordinary solvents, crystallises from boiling alcohol and acetone in stellar aggregates of long plates, becomes yellow at 200° and decomposes at 210°; when rapidly heated, the decomposition takes place at 212—216°.

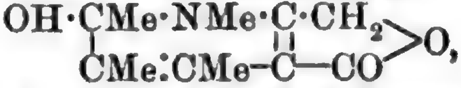
2 : 3 : 4-*Trimethylquinolide*,  $\begin{matrix}CMe:N—C\cdot CH_2\\ | \qquad\quad \| \\ CMe:CMe\cdot C—CO\end{matrix}>O$, produced by treating the oxime of acetonylpropylidenebistetronic acid with glacial acetic acid, crystallises in long needles melting at 152°; it has a neutral reaction and does not interact with acetic anhydride or nitrous acid; its *picrate*, $C_{10}H_{11}O_2N,C_6H_2(NO_2)_3\cdot OH$, separates, on mixing alcoholic solutions of its generators, in yellow needles sintering at 160° and melting at 169°; the *hydrochloride* is readily soluble in water and separates from alcoholic solutions in prisms decomposing at 220°; it is dissociated by water and ether. The *platinichloride*, $(C_{10}H_{11}O_2N)_2,H_2PtCl_6,2H_2O$, crystallises in reddish-yellow prisms.

The base is stable towards cold alkali solutions, but, on warming, hydrolysis occurs, and by the use of barium hydroxide the *barium* salt of 2 : 3 : 4-*trimethyl*-6-*hydroxymethylquinolinic acid* is produced, this substance separating from water in nodular aggregates; the *silver* salt, $C_{10}H_{12}O_3NAg$, crystallises in sparingly soluble needles; the free *acid*, obtained by adding sulphuric acid to a solution of the barium salt, crystallises in colourless prisms and melts at 169°, becoming reconverted into the original lactone base; this change is also slowly induced by boiling with water or dilute hydrochloric acid.

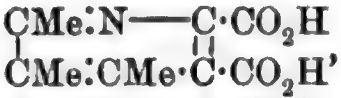


2 : 3 : 4-*Trimethylquinolide methiodide*, $$\begin{array}{l} \mathrm{CMe{:}NMeI\cdot C\cdot CH_2} \\ \mathrm{CMe{:}CMe{-}C{-}CO} \end{array} \!\!> \mathrm{O},$$ prepared by heating its generators at 100°, crystallises from hot water in yellow prisms melting at 116—120°; at higher temperatures, it dissociates into its generators; the *platinichloride*, $(C_{11}H_{13}O_2N)_2,H_2PtCl_6$, produced by treating the iodide successively with silver chloride and platinic chloride, crystallises from hydrochloric acid in prisms exhibiting cruciform twinning and melting at 225°.





The *pseudo-ammonium base*, $$\begin{array}{l} \mathrm{CMe\cdot NMe{-\!-}C\cdot CH_2} \\ \mathrm{CMe\cdot CMe(OH)\cdot C{-}CO} \end{array} \!\!> \mathrm{O} \text{ or } \begin{array}{l} \mathrm{OH\cdot CMe\cdot NMe\cdot C\cdot CH_2} \\ \mathrm{\quad\;\; CMe{:}CMe{-}C{-}CO} \end{array} \!\!> \mathrm{O},$$ is the final product of the action of alkali hydroxides or carbonates on the preceding iodide; when, however, the reaction is performed by means of moist silver oxide, there is evidence that an intermediate compound is formed having the alkaline properties of a true ammonium hydroxide. The pseudo-base crystallises from water in colourless, monoclinic plates containing $3H_2O$; it becomes anhydrous at 100°, changes colour to yellow at 230° and decomposes at 259°. This compound does not react with hydroxylamine or phenylhydrazine; methyl iodide or hydrochloric acid converts it into the corresponding salt of the true ammonium derivative.

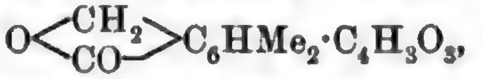


2 : 3 : 4-*Trimethylquinolinic acid*, $$\begin{array}{l} \mathrm{CMe{:}N{-\!-}C\cdot CO_2H} \\ \mathrm{CMe{:}CMe\cdot C\cdot CO_2H} \end{array},$$ obtained by oxidising 2 : 3 : 4-trimethyl-6-hydroxymethylquinolinic acid with an alkaline solution of potassium permanganate, crystallises from water or alcohol in prisms, and melts at 194—195° with evolution of carbon dioxide; at higher temperatures it again becomes solid and finally boils at 250°. The *silver* salt is a gelatinous precipitate, the *lead* salt crystallises in needles or prisms.

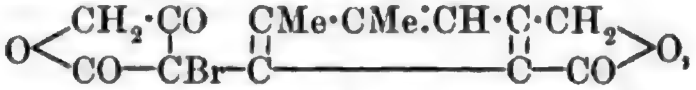
2 : 3 : 4-*Trimethylnicotinic acid*, $C_5NHMe_3\cdot CO_2H$, produced by heating the preceding acid at 160—170°, crystallises from alcohol in prisms melting at 257°; its carboxyl group is probably situated in the *m*-position with respect to the nitrogen, but this is not known with certainty.

2 : 4-Dimethylpyridine-3 : 5 : 6-tricarboxylic acid, prepared by oxidising the dicarboxylic acid with hot permanganate solution, melts at 218° and is identical with the product obtained by Hantzsch from lutidinetricarboxylic acid; when heated with water at 170°, it loses one carboxyl group and becomes converted into 2 : 4-dimethylpyridine-3 : 5-dicarboxylic acid. Further oxidation of the tricarboxylic acid leads to the production of γ-picolinetetracarboxylic acid and pyridinepentacarboxylic acid; these compounds, when heated with glacial acetic acid at 130°, lose the two carboxyl groups in the ortho-position with respect to the nitrogen atom, yielding γ-picoline-3 : 5-dicarboxylic acid and pyridine-3 : 4 : 5-tricarboxylic acid respectively.

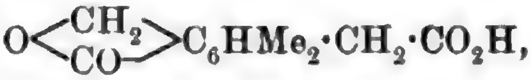
*iso*Acetophoroneoxime, dimethyl*cyclo*hexenoneoxime, and methyl*cyclo*hexenoneoxime, when heated with hydrochloric acid, lose the elements of water and become converted into 5-amino-1 : 2 : 3-trimethylbenzene, *s*-xylidine, and *m*-toluidine respectively, this transformation being in each case accompanied by a shifting of one methyl group from the complex $>CMe_2$ to an adjacent carbon atom of the nucleus.

Dimethylphthalidetetronic acid,  $\mathrm{O}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CO}}{>}\mathrm{C_6HMe_2{\cdot}C_4H_3O_3}$, produced from dimethyldihydrophthalidetetronic acid (see Abstr., 1901, i, 285) by warming with concentrated sulphuric acid containing 1—2 per cent. of sulphur trioxide, is a monobasic acid crystallising from boiling alcohol or water in aggregates of needles and melting at 289°; it develops with ferric chloride a cherry-red coloration.

Dimethylphthalidebromotetronic acid,



obtained by treating the preceding substance with bromine in the presence of water, crystallises from chloroform and petroleum in colourless prisms or plates and decomposes at 178—179°; when heated with dilute hydrochloric acid or alcohol, it gives rise to the original compound.

Dimethylphthalideacetic acid,  $\mathrm{O}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CO}}{>}\mathrm{C_6HMe_2{\cdot}CH_2{\cdot}CO_2H}$, results from the potash fusion of dimethylphthalidetetronic acid and crystallises from dilute alcohol in white needles melting at 212—214°; both these substances are monobasic acids.

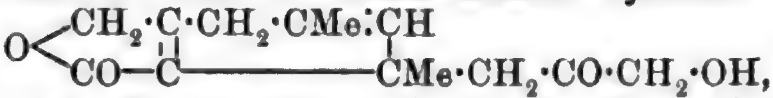
Dimethylhomophthalcarboxylic acid, produced from the preceding compound by first hydrolysing the lactone rings with concentrated potassium hydroxide solution and then oxidising the product with cold potassium permanganate solution, crystallises from hot water in short prisms containing $2H_2O$ and melting at 218—220°; the anhydrous acid melts at 221°. When titrated with phenolphthalein, the substance behaves as a tribasic acid; it yields sparingly soluble lead and *silver* salts, the latter having the composition $C_{12}H_{10}O_6Ag_2$.

Benzenepentacarboxylic acid, produced when the preceding oxidation is carried out with excess of the reagent, crystallises from hot water in needles containing $5H_2O$ and melting at 238°. A compound said to have the same composition was described by Friedel and Crafts as an amorphous substance containing $6H_2O$. The crystalline acid has, however, all the required properties; its neutral potassium salt, on distillation with calcium carbonate, yields a mixture of benzene and diphenyl; the free acid, when heated at 240—250°, furnishes an anhydride and at 270—300° loses carbon dioxide, giving rise to the anhydride of pyromellithic acid.

Dipotassium trihydrogen benzenepentacarboxylate,

$$C_6H(CO_2K)_2(CO_2H)_3,4H_2O,$$

obtained by adding dilute sulphuric acid to a solution of the normal salt, crystallises in plates. *Potassium tetrahydrogen benzenepentacarboxylate,* $C_6H(CO_2H)_4{\cdot}CO_2K,2\frac{1}{2}$ or $3H_2O$, crystallises in felted, silky needles.

Dimethyldihydrophthalidetetronic acid, when heated with 20 per cent. hydrochloric acid at 170°, loses carbon dioxide and becomes converted into a neutral *compound*, $C_{13}H_{14}O_3$, which crystallises from dilute alcohol in white needles or prisms melting at 139°; this substance gives no ferric chloride coloration, but yields an oxime melting at 172° and dissolving in hydrochloric acid or dilute sodium hydroxid solution. The formula  $O{<}\begin{matrix}CH_2\cdot C\cdot CH_2\cdot CMe{:}CH \\ CO{-}C{-\!-\!-\!-}CMe\cdot CH_2\cdot CO\cdot CH_2\cdot OH\end{matrix}$, is suggested for the intermediate product of this reaction, the substance, $C_{13}H_{14}O_3$, actually isolated being an *eso*-anhydride produced by the elimination of 1 mol. of water. G. T. M.

Aromatic Glutaric Acids. By SAMUEL AVERY (*Amer. Chem. J.*, 1902, **28**, 48—59).—[With H. C. PARMELEE.]—β-p-*Tolylglutaric acid*, obtained by hydrolysing the ester formed by the condensation of ethyl *p*-tolylacrylate with ethyl sodiomalonate, crystallises from hot water in transparent, oblique prisms, melts at 165—167°, and is soluble in ethyl acetate or chloroform. The *silver*, *copper*, and *calcium* salts were prepared and analysed The *anhydride*, prepared by heating the acid above its melting point or by treating it with hot acetyl chloride, forms feathery crystals and melts at 153°. By the action of aniline on the anhydride, β-p-*tolylglutaranilic acid* is obtained which crystallises in white needles and melts at 194—196°; its *silver* salt was analysed. If the anilic acid is heated above its melting point, β-p-*glutaranil* is produced, which crystallises in long needles and melts at 174·5°.

[With M. C. GERE.]—β-*m*-Nitrophenylglutaric acid (Knoevenagel, Abstr., 1899, i, 214) was prepared by hydrolysis of the tricarboxylic ester formed by the action of ethyl sodiomalonate on ethyl *m*-nitrocinnamate; its *silver*, *calcium*, *barium*, and *copper* salts were prepared. The *anhydride*, obtained by the action of boiling acetic anhydride on the acid, forms white, silky crystals and melts at 170·5°. The *anilic acid* melts at 160°; its *silver* salt was prepared and analysed.

[With HAL. T. BEANS.]—By the action of fuming nitric acid on β-phenylglutaric acid, β-p-*nitrophenylglutaric acid* is obtained, which crystallises in hard, short prisms, melts at 237°, and is soluble in alcohol, ethyl acetate, or glacial acetic acid; a smaller quantity of another *substance* is simultaneously produced, which forms light yellow crystals, melts at 175°, and is probably β-*o*-nitrophenylglutaric acid. The *silver*, *calcium*, and *barium* salts of the *p*-acid are described. β-*p*-Nitrophenylglutaric *anhydride*, obtained by the action of boiling acetic anhydride on the acid, forms pale yellow crystals, melts at 122·5°, and is soluble in ethyl acetate. The *dimethyl* ester crystallises in large, nearly colourless, plates and melts at 62°. The *anilic acid* crystallises from dilute alcohol in light, glistening flakes and melts at 120—121°; its *silver* salt was analysed. The *anil* forms white needles and melts at 203°. E. G.

Chrysodiphenic Acid. (2-Phenylnaphthalene-1:2′-dicarboxylic Acid). By CARL GRAEBE and R. GNEHM, jun. (*Ber.*, 1902, **35**, 2744—2746).—*Chrysodiphenic acid* (*2-phenylnaphthalene*-1 : 2′-*dicarboxylic acid*), $CO_2H\cdot C_{10}H_6\cdot C_6H_4\cdot CO_2H$, is formed when Graebe and Hönigsberger's amic acids, $CO_2H\cdot C_{10}H_6\cdot C_6H_4\cdot CO\cdot NH_2$, and

$NH_2 \cdot CO \cdot C_{10}H_6 \cdot C_6H_4 \cdot CO_2H$, are fused with sodium hydroxide for four hours at 210—220°. It melts at 199° (corr.), and is only sparingly soluble in cold water. Acetic anhydride converts it into an anhydride, and direct esterification yields an acid ester. Concentrated sulphuric acid gives rise to a mixture of two monobasic acids. J. J. S.

Lichens and their Characteristic Constituents. VII. By OSWALD HESSE (*J. pr. Chem.*, 1902, [ii], **65**, 537—563. Compare Abstr., 1901, i, 595).—*Usnea ceratina* (Ach.), gathered from Java cinchona bark, contains usnaric acid, *d*-usnic acid, parellic acid, and *ceratin*, which forms small, white crystals, melts at 226°, and gives a purple-violet colour with ferric chloride in alcoholic solution.

Usnea barbata (a) *florida*, from Ceylon cinchona bark, contains *d*-usnic acid, usnaric acid, parellic acid, and usnarin.

Usnea barbata (β) *hirta*, from Ceylon cinchona bark, contains *d*-usnic acid, usnaric acid, barbatic acid, and usnarin.

Alectoria articulata, from Java and Jamaica cinchona barks, contains a small proportion of *d*-usnic acid and a trace of usnaric acid.

Alectoria canariensis, from Jamaica cinchona bark, contains usnaric acid, *d*-usnic acid ($[\alpha]_D$ +489·1° at 15° in chloroform solution).

The formula for usnidic acid is now found to be $C_{14}H_{14}O_6,3H_2O$; when slowly heated, it begins to melt and decompose at 187°, and at 192° is completely melted to a brown mass; when rapidly heated, it melts at 195°. It is slightly soluble in boiling water, from which it crystallises in delicate needles easily soluble in acetone and hot glacial acetic acid, but only sparingly so in dilute acetic acid. With ferric chloride, the aqueous solution gives no coloration, the alcoholic solution gives an intense ink-blue colour. The *potassium* salt crystallises from hot dilute alcohol in light yellow needles; the *sodium* salt, $C_{14}H_{13}O_6Na,2H_2O$, forms small, yellow needles, soluble in cold water with separation of part of the acid, which dissolves completely in hot water. In presence of a slight excess of alkali, the aqueous solution gradually absorbs oxygen, becoming at first green and finally brown. The *barium* salt crystallises in stellate groups of needles containing $3H_2O$; the *silver* salt, obtained as a flocculent, gelatinous precipitate, on addition of silver nitrate to the aqueous solution of the sodium salt, is not changed on boiling, becomes brown on exposure to light, and is easily soluble in aqueous ammonia. When heated in a stream of hydrogen, usnidic acid decomposes into carbon dioxide and *usnidole*, $C_{13}H_{14}O_4$, which sublimes in long, yellow needles, melts at 176°, and gives, with ferric chloride, no colour in aqueous solution, but a blue colour in alcoholic solution.

Usnidic acid is identical with the acid obtained from usnic acid by Salkowski (Abstr., 1901, i, 152) and with the pyrousnitic acid and pyrousnic acid of Paternò (Abstr., 1882, 1079).

Cornicularia aculeata (Ach.), from the Gerlinger Höhe, between Schloss Solitude and Leonberg (Württemberg), contains rangiformic acid.

Evernia divaricata, from Brand (Vorarlberg), contains no usnic acid (compare Abstr., 1898, i, 522, and Zopf, Abstr., 1901, i, 546).

Evernia prunastri, from Feuerbach, is found to contain usnic acid, which is not present in two specimens from Teinach (Black Forest).

Ramalina yemensis, from *Aspidosperma Quebracho*, Cordoba (Argentine), contains a small proportion of *d*-usnic acid, and an *acid* crystallising in small, white needles from alcohol, sparingly soluble in ether, and giving a purple-red colour with ferric chloride in alcoholic solution.

Cladonia alcicornis, from the Gerlinger Höhe, contains usnic acid (m. p. 196°).

Cetraria pinastri, from Liechtenstein, has been re-examined and its composition confirmed. Stictaurin, which, according to Zopf (*loc. cit.*) is contained in *Sticta desfontainii* (α) *munda* and in *Sticta aurata*, is a mixture of pulvic anhydride and calycin, both of which are optically inactive (compare Salkowski, *loc. cit.*).

Parmelia glabra, from Calmbach, contains lecanoric acid.

The presence of lecanoric acid in *Parmelia sorediata* is confirmed.

Physcia cæsia, from Brand (Vorarlberg) and from Liechtenstein, contains atranorin and zeorin, as stated by Zopf, but no hæmatommic acid is present. Zeorin does not react with phenylhydrazine.

Nephromium lævigatum (α) *genuinum*, from Liechtenstein, contains a small proportion of an *acid*, which is easily soluble in alcohol and gives a greenish-brown coloration with ferric chloride but no coloration with bleaching powder.

Placodium circinatum (α) *radiosum*, from Brand, contains salazic acid.

Placodium gypsaceum, contains no usnic acid (compare Zopf).

Callopisma flavovirescens, from Brand, contains physcion, which melts at 207—208°. Zopf gives m. p. 205°.

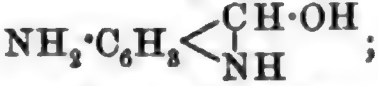
Hæmatomma coccineum var. *abortivum*, from Teinach (Black Forest), contains *coccic acid*, atranorin, *hæmatommin*, and *hæmatommidin*. Coccic acid, $C_{12}H_{16}O_{10},3H_2O$, crystallises in delicate, white needles, becomes brown at 250°, and melts and decomposes at 262—264°, gives a blue coloration with ferric chloride in alcoholic solution, no coloration with bleaching powder, dissolves in cold concentrated sulphuric acid to a colourless solution which on warming becomes green to violet, reddens alcoholic litmus solution, and dissolves easily in aqueous sodium carbonate solution. Hæmatommin, $C_{10}H_{16}O$ or $C_{20}H_{32}O_2$, forms a white, crystalline powder, melts at 143—144°, is sparingly soluble in ether, alcohol, or acetic acid, insoluble in aqueous potassium hydroxide or ammonia, and gives no colour reaction with ferric chloride or bleaching powder. Hæmatommidin crystallises in small, white needles, from hot alcohol in characteristic ball-like aggregates, melts at 194—196°, is easily soluble in ether, benzene, acetone, or hot glacial acetic acid, insoluble in aqueous potassium hydroxide or ammonia, gives no coloration with ferric chloride or bleaching powder, and dissolves in cold concentrated sulphuric acid to a yellow solution which becomes brown on warming.

Ochrolechia pallescens (γ) *parella*, from Sandstein, near Trieste, and from Norway, contains *ochrolechiasic acid*, but no lecanoric acid (compare Schunck, *Annalen*, 1845, **54**, 274).

Ochrolechiasic acid forms microscopic, white crystals, which lose 10 per cent. water of crystallisation at 120° and melt at 280°; it is much less soluble than parellic acid in hot alcohol, dissolves easily in hot glacial acetic acid, but is only sparingly soluble in ether. The alcoholic solution gives a purple coloration with ferric chloride; the solution in concentrated sulphuric acid becomes reddish-brown on warming. It is easily soluble in aqueous potassium hydroxide and is precipitated by addition of hydrochloric acid. On boiling with aqueous barium hydroxide, barium carbonate is precipitated and there remains in solution an amorphous substance which in alcoholic solution gives a purple coloration with ferric chloride. G. Y.

2:4-Dinitrobenzaldehyde. II. By FRANZ SACHS and R. KEMPF (*Ber.*, 1902, **35**, 2704—2717. Compare this vol., i, 376 and 377).—2:4-*Dinitrobenzylidene-o-toluidine* crystallises from amyl alcohol in long, lustrous, yellow needles and melts at 153·5° (corr.); 2:4-*dinitrobenzylidenebenzidine* crystallises from xylene in small, thin, striated plates of a reddish colour and melts at 186°, and the *bis*-2:4-*dinitrobenzylidenebenzidine* crystallises with 1 mol. of nitrobenzene in yellowish-red, silky needles or with 1 mol. of benzene in bright yellow, slender needles, losing the nitrobenzene or benzene of crystallisation at 120—130° and melting at 246°. The *semicarbazone* crystallises in long, slender needles and melts and decomposes at 265°.

Attempts to prepare the aldehyde or 2:4:6-trinitrobenzaldehyde by the electrolytic oxidation of the corresponding nitrotoluenes led only to the formation of the acids.

When reduced with ammonium sulphide, the aldehyde yields the *compound* $C_7H_8ON_2$, which crystallises in yellow laminæ, melts at 152·5° (corr.), and probably has the constitution  $NH_2\cdot C_6H_3<\begin{matrix}CH\cdot OH\\ | \\ NH\end{matrix}$; the *diacetyl* derivative crystallises in lustrous needles and melts at 235·5° (corr.), and, when treated with phenylhydrazine in glacial acetic acid solution, yields *diacetyldiaminobenzylidenephenylhydrazone*, which separates from nitrobenzene or acetic acid in yellow crystals melting and decomposing between 246° and 252° (corr.).

2:4-*Nitroaminobenzaldehydesemicarbazone*, obtained when the corresponding oxime (*loc. cit.*) is treated with semicarbazide, is a yellowish-red, crystalline powder which decomposes between 220° and 300° without melting; the O,N-*diacetyl* derivative of the oxime crystallises in almost colourless needles and melts at 174° (corr.).

When *o*-nitrobenzylideneaniline is exposed in benzene solution to a strong light for 8 days, a 44 per cent. yield of *o*-nitrosobenzoylanilide is obtained; 2:4-dinitrobenzylideneaniline similarly yields two undetermined *compounds* melting respectively at 289° (corr.) and 180·5° (corr.). R. H. P.

Condensation of Nitromethane with Aromatic Aldehydes. By LOUIS BOUVEAULT and ANDRÉ WAHL (*Compt. rend.*, 1902, **135**, 41—43).—Nitromethane readily condenses with aromatic aldehydes in presence of sodium methoxide and methyl alcohol, forming derivatives of the type $OH\cdot CHR\cdot CH\colon NO\cdot ONa$; these dissolve without change in water but are decomposed by acids with liberation of the corresponding nitroalcohol, which, at the moment of its formation, is partially dehydrated, yielding compounds of the type $CHR\colon CH\cdot NO_2$. The dehydration is complete if the salts are boiled with zinc chloride dissolved in glacial acetic acid. Anisaldehyde yields p-*methoxy-ω-nitrostyrene* in yellow needles which melt at 80° and are reduced by zinc and acetic acid to p-*methoxyphenylacetaldoxime*, melting at 112°. Piperonylaldehyde yields *piperonylidenenitromethane* in yellow needles melting at 159°; when reduced, it yields the *oxime* of *homopiperonylaldehyde* melting at 120°. Furfuraldehyde yields *furfurylidenenitromethane*, which melts at 74° and boils at 135° under 20 mm. pressure; the *homofurfuraldoxime* which it yields on reduction forms long needles melting at 61—62° and boiling at 120—130° under 25 mm. pressure.

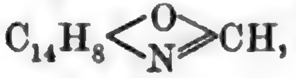
The sodium derivative of the nitroalcohol obtained in this way from *o*-nitrobenzaldehyde is not dehydrated by zinc chloride, but when distilled in a vacuum it yields *o*-ω-dinitrostyrene, melting at 106—107° and boiling at about 200° under 20 mm. pressure. C. H. B.

Constitution of Auramine and the Salts of Phenyliminobenzophenone. By Carl Graebe (*Ber.*, 1902, **35**, 2615—2621. Compare Abstr., 1899, i, 702).—The close resemblance existing between the salts of auramine and phenyliminobenzophenone renders the quinonoid constitution of the former very doubtful, since it is not possible to formulate the latter on this type. The production of a very stable hydrated hydrochloride of phenyliminobenzophenone is not decisive evidence in favour of the quinonoid view (compare Dimroth and Zoeppritz, this vol., i, 292), since anhydrous salts of this imine may be readily obtained. The anhydrous *hydrochloride*, $CPh_2\colon NPh,HCl$, prepared by leading hydrogen chloride into a benzene solution of the imine, is a pale yellow precipitate melting at 190°; it dissolves in chloroform to an intensely yellow solution. The *hydriodide*, $CPh_2\colon NPh,HI$, produced by shaking the benzene solution of the imine with dilute hydriodic acid, melts and decomposes at 185°. The *methiodide*, formed by heating its generators on the water-bath, separates in deep yellow crystals melting at 202°; when heated with alkali hydroxides or carbonates, it is hydrolysed into benzophenone and methylaniline. *Auramine methiodide*, $(NMe_2\cdot C_6H_4)_2C\colon NH,MeI$, obtained either by mixing its generators at the ordinary temperature or by heating them in benzene solution at 100°, separates in deep yellow crystals and melts at 235—240°; it dissolves in hot water or in hydrochloric acid, but is insoluble in benzene. A trimethiodide, produced by the action of excess of methyl iodide, separates in yellow crystals and melts at 165°.

The monomethiodide must be regarded as the hydriodide of methylauramine, for it yields this substance on treatment with dilute sodium hydroxide solution; the new base closely resembles auramine and melts at 130°. Phenylauramine may be readily prepared by heating tetramethyldiaminobenzophenone with aniline at the boiling point of the latter; its *hydriodide*, produced by double decomposition from potassium iodide and the chloride, separates in anhydrous, yellow crystals melting at 242°; the *methiodide*, $(NMe_2\cdot C_6H_4)_2C\colon NPh,MeI$, obtained by heating an equivalent proportion of its generators in benzene solution at 100°, separates in red crystals melting at 214°; on hydrolysis, it yields tetramethyldiaminobenzophenone and methyl aniline, this result indicating that in the methiodide the methyl iodide is attached to the iminic nitrogen. When phenylauramine is warmed with excess of methyl iodide at 100°, a *trimethiodide*, $(NMe_3I\cdot C_6H_4)_2C\colon NPh,MeI$, is produced which separates in ruby-red crystals; this salt, when dried at 100°, loses rather more than one mol. of methyl iodide, at 120° a second mol. is removed, and the composition of the product approximately corresponds with that of the monomethiodide. G. T. M.

Derivatives of Desylamine and of Phenanthraquinone. By ROBERT PSCHORR and FRITZ BRÜGGEMANN (*Ber.*, 1902, **35**, 2740—2744. Compare Gabriel and Neumann, Abstr., 1890, 890).—Desylamine, $COPh\cdot CHPh\cdot NH_2$, may be obtained by the reduction of an alcoholic solution of benzilmonoxime with stannous chloride and concentrated hydrochloric acid. The hydrochloride crystallises in needles on the addition of ether to its alcoholic solution and melts at 243° (corr.), not at 209°. Its solubility in hot alcohol is 1 : 7, in cold alcohol 1 : 12, and in cold water 1 : 20. The free base melts at 109° (corr.) and crystallises from ether in needles. It combines with phenylcarbimide, yielding *desylphenylcarbamide* melting at 174—175° (corr.). *Desylaminephenylhydrazone* crystallises from acetic acid in small, yellow needles melting at 226—227° (corr.).

The *benzoyl* ester of phenanthraquinoneoxime crystallises in needles melting at 174—175° (corr.), and when reduced yields 9 : 10-aminophenanthrol. The additive *compound* of phenanthraquinoneoxime and phenylcarbimide crystallises from benzene in needles melting at 127—128°, and on reduction yields aminophenanthrol.

When methylated, the oxime yields the *anhydride* of phenanthraquinoneoxime methyl ether,  $C_{14}H_8<\substack{O\\N}>CH$, melting at 145—146° (compare Moldauer, Abstr., 1897, i, 42). J. J. S.

Crystallography of the Borneols and of their Esters and of Chloral and Bromal Bornylate. By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], **27**, 683—689).—In preparing artificial *d*-borneol from the mixture of this with *l-iso*borneol which is obtained by the hydrogenisation of camphor, the author makes use of the fact that the *iso*borneol is much more rapidly oxidised by chromic acid than is *d*-borneol.

The succinate of artificial *d*-borneol crystallised from light petroleum forms hexagonal plates modified by rhombohedral faces; crystallised from methyl alcohol, it forms rhombic prisms [$a:b:c = 0.91633:1:0.77067$]. *l*-Bornyl succinate is perfectly similar to the *d*-compound. The succinates of the *iso*borneols form hexagonal plates isomorphous with those of the borneols, but no rhombic prisms have been obtained in the case of the *iso*borneols. The crystals of *r*-bornyl succinate differ from those given above, but the angles could not be measured on account of the opacity of the crystals. *d*-Bornyl phthalate crystallises in the rhombic system [$a:b:c = 0.85605:1:2.3407$]. *l*-Bornyl phthalate has the same crystalline form, but the author believes that plagiohemihedry is also present.

The campholates of chloral are not isomorphous with those of bromal, although the campholates and *iso*campholates are in each case isomorphous. Bromal campholate and *iso*campholate crystallise in monoclinic prisms [$a : b : c = 1\cdot1697 : 1 : 1\cdot0600$; $\beta = 96°15'$]. A. F.

Crystallography of the Brominated Derivatives of Benzylidenecamphor and of Benzylcamphor. By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], **27**, 679—681).—Bromobenzilidenecamphor crystallises in rhombic prisms [$a : b : c = 0\cdot59494 : 1 : 0\cdot3994$]. Bromobenzylcamphor crystallises in rhombic prisms [$a : b : c = 0\cdot9462 : 1 : 0\cdot8846$]; *o*-bromobenzylidenecamphor crystallises in monoclinic prisms [$a : b : c = 0\cdot97679 : 1 : 0\cdot5585$; $\beta = 107°28'$]. *p*-Bromobenzylidenecamphor forms rhombic prisms [$a : b : c = 0\cdot8068 : 1 : 1\cdot455$]. No hemihedral faces have been observed in the case of the above compounds, but, nevertheless, their internal structure is asymmetric. A. F.

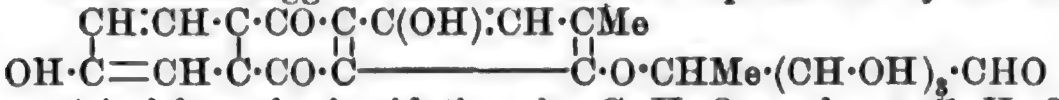
Fenchene. By OTTO WALLACH (*J. pr. Chem.*, 1902, [ii], **65**, 586—596).—Polemical. A reply to Kondakoff (this vol., i, 478).
G. Y.

Cinnamon Oil from Ceylon. By HEINRICH WALBAUM and O. HÜTHIG (*J. pr. Chem.*, 1902, [ii], **66**, 47—58).—In addition to cinnamaldehyde, the authors have obtained the following from cinnamon oil from Ceylon:—Methyl amyl ketone, pinene, phellandrene, cymene, benzaldehyde, linalool, caryophyllene, cuminaldehyde, and eugenol. They also found indications of the presence of a higher fatty aldehyde (probably nonylaldehyde), furfuraldehyde, phenylpropaldehyde, and *iso*butyric acid (as an ester). R. H. P.

Sugars from Crocin and Picrocrocin. By JAROSLAV KASTNER (*Zeit. Zuckerind. Böhm.*, 1902, **26**, 538—541).—A careful examination of the sugar produced by the hydrolysis of crocin and picrocrocin has shown that in each case it consists of dextrose only. E. G.

Constitution of Aloins: Comparison with that of Glucosides. By EUGÈNE LÉGER (*Compt. rend.*, 1902, **134**, 1584—1586. Compare this vol., i, 549).—Besides *iso*hydroxymethylchrysasin (trihydroxymethylanthraquinone), there is formed in the action of sodium peroxide on barbaloin and its isomerides, formic acid and a lævorotatory substance having the composition of an aldopentose.

The author suggests that barbaloin is represented by the expression



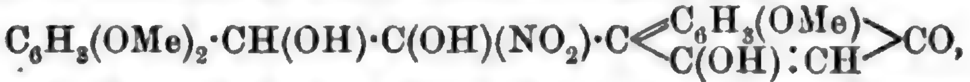
$$\begin{array}{l} \quad \mathrm{CH{:}CH\cdot C\cdot CO\cdot C\cdot C(OH){:}CH\cdot CMe} \\ \mathrm{OH\cdot C{=}CH\cdot C\cdot CO\cdot C\text{————}C\cdot O\cdot CHMe\cdot(CH\cdot OH)_3\cdot CHO} \end{array}$$

; the empirical formula should then be $C_{21}H_{20}O_9$, and not $C_{16}H_{16}O_7$ which has been previously used. Further, chlorobarbaloin has the formula $C_{21}H_{16}O_9Cl_4$, and its acetyl derivative $C_{21}H_{11}O_9Cl_4Ac_5$; the mol. weight of the last-mentioned substance (in benzene) is in agreement with this formula. Attention is drawn to the fact that these aloins resemble glucosides in constitution, but, unlike them, are not hydrolysable by dilute acids.

In ethyl acetate, barbaloin has $[\alpha]_D$ −10·4°, in water +21·4°; *iso*barbaloin has $[\alpha]_D$ −19·4° in ethyl acetate, but is inactive in aqueous solution. It is suggested that *iso*barbaloin differs from barbaloin in the position of attachment of the sugar group to the anthraquinone nucleus; in the former, the point of attachment is probably at position 6.

Both nataloin and homonataloin are optically active; in ethyl acetate, nataloin has $[\alpha]_D$ $-107\cdot7°$, and homonataloin $[\alpha]_D$ $112\cdot6°$; it seems most probable that these substances are respectively represented by the formulæ $C_{23}H_{26}O_{10}$ and $C_{22}H_{24}O_{10}$. K. J. P. O.

The Degradation of Brazilin. By Stanislaus von Kostanecki and Ludwig Paul (*Ber.*, 1902, **35**, 2608—2611. Compare this vol., i, 482, and Gilbody and Perkin, Trans., 1902, **81**, 1049).—The oxidation product, $C_{19}H_{18}O_6$, of trimethylbrazilin, when treated with cold nitric acid yields the nitrogenous substance $C_{19}H_{19}O_9N$, which, on warming with solutions of the alkali hydroxides, becomes decomposed into *p*-methoxysalicylic acid and two neutral nitro-compounds. These substances, 6-nitrohomoveratrol and *tetramethoxydinitrodibenzyl*, are separated by treatment with alcohol in which solvent the latter is insoluble. The dinitro-compound crystallises from glacial acetic acid or benzene and alcohol in white needles and melts at 206°. The initial product of nitration is assumed to have the formula



$$C_6H_3(OMe)_2\cdot CH(OH)\cdot C(OH)(NO_2)\cdot C{<}\begin{matrix}C_6H_3(OMe)\\ C(OH){:}CH\end{matrix}{>}CO,$$

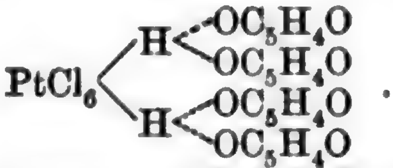
and results from the fission of the indanediole nucleus of the compound $C_{19}H_{18}O_6$, the reaction being accompanied by the addition of a mol. of nitric acid; this nitro-compound should on hydrolysis give rise to *p*-methoxysalicylic and glycollic acids together with 6-nitrohomoveratrol; its precise relationship to the dibenzyl derivative has not yet been definitely determined. G. T. M.

Oxonium Theory. By Alfred Coehn (*Ber.*, 1902, **35**, 2673—2677).—The electrolysis of a solution of dimethylpyrone hydrochloride seems to decide whether this substance is a molecular compound or a true salt, since in the latter case the dimethylpyrone will migrate along with the hydrogen as a complex positive ion to the cathode. This actually occurs when a solution of 60 grams of dimethylpyrone hydrochloride in 250 grams of 20 per cent. hydrochloric acid is electrolysed, and the accumulation of dimethylpyrone at the cathode takes place both when the cathode is separated from the solution by a membrane and when no membrane is present. In the experiments, the effect of diffusion was allowed for, and the disappearance of dimethylpyrone from the neighbourhood of the anode was also observed.

A. H.

Constitution of Oxonium Salts. By Alfred Werner (*Annalen*, 1902, **322**, 296—351. Compare this vol., ii, 50).—The hypothesis of supplementary valency is employed in explaining the production of the oxonium compounds.

Pyrone, when treated with platinic chloride in concentrated aqueous solution, gives rise to the crystalline *platinichloride*, $C_{20}H_{14}O_8,H_2PtCl_6$, which separates in flesh-coloured leaflets. The formation of this compound, which contains four mols. of pyrone, is not readily explicable on the assumption that it contains quadrivalent oxygen. According to the author's theory, the combination occurs through the agency of the supplementary valencies of the pyrone oxygen and the hydrogen of the chloroplatinic acid, the substance produced having the coordination formula :



Dimethylpyrone cupric chloride, $C_7H_8O_2CuCl_2$, separates in brownish-yellow needles on adding dimethylpyrone to a saturated cupric chloride solution, and similar compounds are obtained with other metallic chlorides. Their formation is assumed to be due to the supplementary valency of the metallic radicle and the pyrone oxygen, the copper compound having the formula $O{\cdot}C_7H_8O{\cdots\cdots}CuCl_2$.

[With KALKMANN.]—The hexacarbaminochromic salts first discovered by Sell have been re-examined from the author's standpoint and the following derivatives are described.

The *bromide*, $[Cr(CON_2H_4)_6]Br_3,3H_2O$, prepared by treating the corresponding chloride with potassium bromide in aqueous solution, crystallises in pale green, soluble needles ; the electrical conductivity at 25° is $\mu_{125} = 290{\cdot}18$ and $\mu_{1000} = 335{\cdot}0$.

The *iodide*, $[Cr(CON_2H_4)_6]I_3$, also obtained from the chloride, crystallises in lustrous, bluish-green needles ; it is more stable than the other halogen salts, and may be heated at the temperature of the water-bath without undergoing decomposition ; its electrical conductivity at 25° is $\mu_{125} = 287{\cdot}2$ and $\mu_{1000} = 338{\cdot}7$.

The *thiocyanate*, $[Cr(CON_2H_4)_6](SCN)_3$, formed by double decomposition from the chloride and potassium thiocyanate, crystallises from water in green needles ; the electrical conductivity at 25° is $\mu_{125} = 269{\cdot}61$ and $\mu_{1000} = 325{\cdot}55$.

The double salt (*hexacarbaminochromic chromihexathiocyanate*), $[Cr(CON_2H_4)_6],[Cr(SCN)_6]$, is produced by allowing a solution of the preceding salt to remain for four weeks, or more rapidly by heating the salt either alone or in solution, the decomposition of the dry compound at 90° being completed in four minutes ; it is also obtained by mixing solutions of the preceding compound and chromic thiocyanate. The product is an amorphous, pale red powder insoluble in water and the other ordinary solvents.

The hexacarbaminochromic chloride, $[Cr(CON_2H_4)_6]Cl_3,3H_2O$, from which the preceding salts are prepared, is produced by treating the product, $Cr(CON_2H_4)_6(Cr_2O_7)Cl,6H_2O$, of the action of chromyl chloride on carbamide with moist lead chloride ; it crystallises in pale green needles belonging to the monoclinic system and decomposes at 155° ; its electrical conductivity at 25° is $\mu_{125} = 296{\cdot}52$ and $\mu_{1000} = 340{\cdot}47$.

The *nitrite*, $[Cr(CON_2H_4)_6](NO_2)_3$, is produced by mixing solutions of the chloride with sodium nitrite or the fumes evolved from arsenious oxide and nitric acid ; it closely resembles the chloride ; its electrical conductivity at 25° is $\mu_{125} = 269{\cdot}7$ and $\mu_{1000} = 324{\cdot}2$.

The *cyanide*, $[Cr(CON_2H_4)_6](CN)_3,5\frac{1}{2}H_2O$, also produced by double decomposition, crystallises in dark-green needles; it is very unstable, melts at 75°, and has an odour of hydrogen cyanide.

Hexacarbaminochromic chromihexacyanide,

$$[Cr(CON_2H_4)_6]CrCy_6,7H_2O,$$

slowly separates from a solution of the preceding cyanide in the form of small, greenish-yellow, sphenoid crystals; it still contains the carbaminochromium complex, yielding the characteristic nitrate and chloride on treatment with nitric and hydrochloric acids respectively.

The *hexahydrated* salt, $[Cr(CON_2H_4)_6]CrCy_6,6H_2O$, obtained by adding potassium chromicyanide to a solution of hexacarbaminochromic chloride, is a pale green powder insoluble in cold water and dissolving only slowly in the warm solvent.

The *permanganate*, $[Cr(CON_2H_4)_6](MnO_4)_3$, produced from the chloride by the interaction of potassium permanganate, is a dark violet, lustrous precipitate readily decomposed on warming.

The *chloride-sulphate*, $[Cr(CON_2H_4)_6]Cl,SO_4,2H_2O$, prepared by mixing solutions of the chloride and a soluble sulphate, crystallises from hot water in lustrous, greenish-blue needles rapidly decomposing on exposure.

The *hydrogen sulphate*, $[Cr(CON_2H_4)_6]H(SO_4)_2,3H_2O$, obtained by adding excess of sulphuric acid to a solution of the preceding salt, crystallises from water acidified with this acid in pale green, prismatic needles.

The *double* salt, $[Cr(CON_2H_4)_6][CO(NO_2)_4(NH_3)_2]_3,3H_2O$, prepared by adding hexacarbaminochromic chloride to a concentrated solution of diammoniocobaltic tetranitrite, separates as a yellowish-brown precipitate which, when crystallised from water in small portions, forms dark yellow needles with a golden lustre decomposing at 100°.

The *double* salt, $[Cr(CON_2H_4)_6][CO(NO_2)_4(NH_3)_2]_2Cl,3H_2O$, produced by reversing the order of mixing employed in the preceding preparation, is a more soluble compound crystallising in slender, pale yellow needles.

The *polysulphide*, $C_6O_6N_{12}H_{24}CrS_6$, is an amorphous, dark green precipitate, obtained by treating the chloride with yellow ammonium sulphide.

[With A. GUBSER.]—The two isomeric hydrated chromium bromides, $CrBr_3,6H_2O$, described by Recoura (Abstr., 1890, 1063) were shown by determinations of the electrical conductivity to be structurally dissimilar.

The green modification, *dibromotetra-aquochromium bromide*,

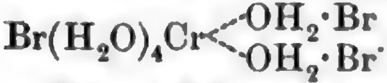
$$[(OH)_4CrBr_2]Br,2H_2O,$$

behaves as a salt containing two ions; the values of μ_{125} vary from 70·7 to 79·5. This compound, however, undergoes hydrolytic dissociation much more rapidly than the corresponding green chloride, and hence the amount of bromine precipitable by silver nitrate is greater than that demanded by the formula.

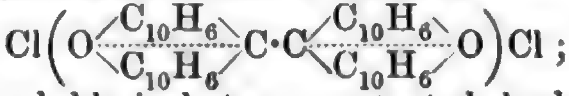
The blue modification, *hexa-aquochromium bromide*, $[Cr(OH_2)_6]Br_3$, is extremely hygroscopic, and, contrary to Recoura's description, is readily soluble in alcohol; it behaves as a salt containing 4 ions, μ_{125} being 173. The whole of its halogen is precipitable by silver nitrate even in cold solutions.

Dibromotetra-aquochromium diaminocobaltitetranitrite,
$[Br_2Cr(OH_2)_4][(NH_3)_2(NO_2)_4]$,
produced by mixing together warm solutions of diaminocobaltic tetranitrite and the green chromium bromide, is precipitated in dark green crystals readily soluble in water, alcohol, or acetone.

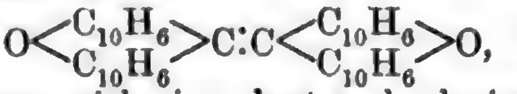
The *double* salt, $[OH_2{\cdot}CrBr_5]Rb_2$, prepared by evaporating down in a current of hydrogen bromide a solution of rubidium bromide, RbBr, and the green chromium bromide, is a brownish-violet, crystalline compound, dissolving in water to a red solution, the colour of which rapidly changes to green. A green double salt has also been obtained, but its composition is not yet ascertained. The transformation of the green hydrate into its blue isomeride is thus indicated according to the theory of supplementary valency, $Br(H_2O)_4CrBr_2 + 2OH_2 =$


$$Br(H_2O)_4Cr{<}\begin{matrix}OH_2{\cdot}Br\\ OH_2{\cdot}Br\end{matrix}$$

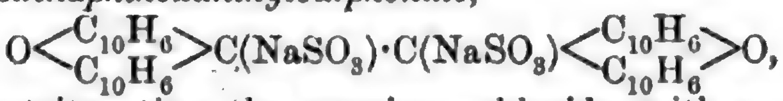
Chloral-β-dinaphthyleneoxide, when oxidised with manganese dioxide and hydrochloric acid in hot glacial acetic acid solution, yields a reddish-brown salt, *bisdinaphthoxanthoxonium chloride*,


$$Cl\left(O{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}C{\cdot}C{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}O\right)Cl;$$

this substance is soluble in hot concentrated hydrochloric acid and separates in small, red crystals with a green reflex; in this form, it has the composition $C_{42}H_{24}O_2Cl_2,HCl,4H_2O$. The *methyl ether*, $C_{44}H_{30}O_4$, is readily produced by boiling the salt with methyl alcohol; the *ethyl ether*, $C_{46}H_{34}O_4$, is prepared in a similar manner; these substances melt respectively at 158° and 147°, and are reconverted into yellow oxonium salts by the action of mineral acids.

Bisdinaphthoxanthylene,  $O{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}C{:}C{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}O$, prepared by reducing the preceding ethers with zinc dust and glacial acetic acid, crystallises in white needles which commence to decompose at 270° but do not melt below 300°; halogens or nitrous fumes reconvert it into oxonium salts.

Sodium bisdinaphthoxanthylsulphonate,


$$O{<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}C(NaSO_3){\cdot}C(NaSO_3){<}\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}{>}O,$$

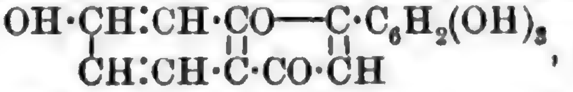
produced by triturating the oxonium chloride with a concentrated solution of sodium hydrogen sulphite, crystallises from hot water either in long, white needles or thin, monoclinic plates; it decomposes at 100°, changing into a red substance which is probably an oxonium sulphite.

The *potassium* salt, $C_{42}H_{24}O_8S_2K_2,10H_2O$, crystallises from water in small, nacreous leaflets which become coppery-red at 100°, the coloured product, however, when crystallised from hot water, again regenerates the colourless salt.

Mineral acids convert these sulphonates into the reddish-yellow oxonium salts. G. T. M.

Oxidising Properties of a Pyranol. By Robert Fosse (*Compt. rend.*, 1902, 135, 39—41).—The action of hydriodic acid on dinaphthapyranol does not yield dinaphthapyranoxonium, but the oxonium tri-iodide (1 mol.) and dinaphthapyran (2 mols.). When dinaphthapyranol is boiled with diphenopyranol in presence of acetic acid, the former is reduced to dinaphthapyran, whilst the latter is oxidised to diphenopyrone. C. H. B.

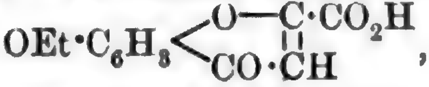
A Tetrahydroxyflavone Dye. By STANISLAUS VON KOSTANECKI and E. PLATTNER (*Ber.*, 1902, **35**, 2544—2546).—2 : 4-*Diethoxy*-3′ : 4′ : 5′-*trimethoxybenzoylacetophenone*, $C_6H_3(OEt)_2 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_2(OMe)_3$, prepared by the action of sodium on a mixture of resacetophenone diethyl ether, and ethyl trimethylgallate, crystallises from a mixture of acetic acid and alcohol in long, pale yellowish needles, which melt at 132·5° and give a dirty red colour with alcoholic ferric chloride. 3 : 3′ : 4′ : 5′-*Tetrahydroxyflavone*,



$$\begin{array}{l} OH \cdot CH{:}CH \cdot CO{-}{-}C \cdot C_6H_2(OH)_3 \\ \;\;\;\;\;\;\; CH{:}CH \cdot C \cdot CO \cdot CH \end{array}$$

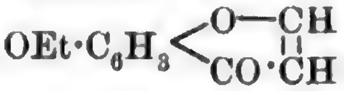
, prepared by the action of hydriodic acid on the preceding compound and purified by conversion into the methyl ether, crystallises from hot dilute alcohol in white needles, with $1H_2O$, and melts and decomposes at 340°. The *tetramethyl ether*, $C_{19}H_{18}O_6$, crystallises in needles and melts at 191—192°. The *tetra-acetyl* compound, $C_{23}H_{18}O_{10}$, crystallises from alcohol in snow-white flakes and melts at 215°. T. M. L.

2-Hydroxychromone. By E. DAVID and STANISLAUS VON KOSTANECKI (*Ber.*, 1902, **35**, 2547—2549).—*Ethyl* 2-*hydroxy*-5-*ethoxybenzoylpyruvate*, $OH \cdot C_6H_4(OEt) \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$, prepared from quinacetophenone monoethyl ether and ethyl oxalate, crystallises from dilute alcohol in needles, melts at 92°, and gives a dirty red colour with alcoholic ferric chloride. 6-*Ethoxychromone-2-carboxylic acid*,



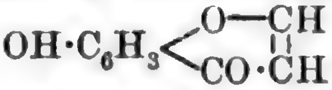
$$OEt \cdot C_6H_3 < \begin{array}{l} O{-}{-}C \cdot CO_2H \\ CO \cdot CH \end{array} ,$$

prepared by the action of hydrochloric acid on an alcoholic solution of the preceding compound, crystallises from alcohol in needles, with $1H_2O$, and melts at 235° with liberation of carbon dioxide. 6-*Ethoxychromone*,



$$OEt \cdot C_6H_3 < \begin{array}{l} O{-}{-}CH \\ CO \cdot CH \end{array}$$

, crystallises from alcohol in glistening, thin tablets, which gradually become dull and crumble and melt at 89—90°. 6-*Hydroxychromone*,



$$OH \cdot C_6H_3 < \begin{array}{l} O{-}{-}CH \\ CO \cdot CH \end{array}$$

, crystallises from dilute alcohol in white needles, melts at 243—244°, and dissolves in dilute sodium hydroxide to a pale yellow solution. The *acetyl* derivative, $C_{11}H_8O_4$, crystallises from dilute alcohol in white needles and melts at 126—127°. T. M. L.

Acyl Derivatives of *iso*Pyromucic Acid: *iso*Pyromucyl Acetate, Benzoate, and Pyromucate. By G. CHAVANNE (*Compt. rend.*, 1902, **134**, 1511—1512).—iso*Pyromucyl acetate*, $COMe \cdot O \cdot C_5H_3O_2$, obtained by heating *iso*pyromucic acid with acetyl chloride or acetic anhydride, boils at 152° under 20 mm. pressure, melts at 28°, is easily soluble in the common organic solvents and very readily so in water, is neutral, and gives no coloration with ferric chloride. It can be easily saponified; with alcohol, in presence of hydrochloric acid, it gives ethyl acetate and *iso*pyromucic acid; with phenylhydrazine, it gives acetylphenylhydrazine, and with aniline, acetanilide. It resembles phenyl acetate rather than the alcoholic acetates (esters).

iso*Pyromucyl benzoate*, $COPh\cdot O\cdot C_5H_3O_2$, obtained by heating *iso*pyromucic acid with benzoyl chloride, crystallises from alcohol in prisms which melt at 85°, cannot be distilled, and is soluble in organic solvents but almost insoluble in water. It can be easily saponified and reacts with alcohol or phenylhydrazine just as the acetate does.

iso*Pyromucyl pyromucate*, $C_4H_3O\cdot CO\cdot O\cdot C_5H_3O_2$, produced by heating *iso*pyromucic acid with pyromucyl chloride at 150° for three hours, is soluble in alcohol, and can be precipitated by water. It melts at 99° and behaves towards reagents just as the acetate does.

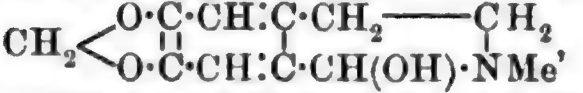
These observations confirm the conclusion already arrived at that *iso*pyromucic acid has a phenolic (enolic) character. J. McC.

Ammonium Compounds. VIII. History of Hydroxydihydro-bases.

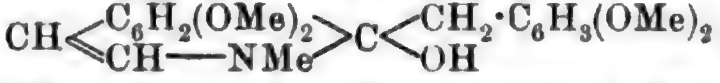
By HERMAN DECKER (*Ber.*, 1902, **35**, 2588—2589).—A summary of the author's views on the action of alkalis on the methiodides of *cyclo*amine bases (compare Abstr., 1893, i, 115). T. M. L.

Ammonium Compounds. IX. Theory of Hydroxydihydrobases.

By HERMAN DECKER (*Ber.*, 1902, **35**, 2589—2593).—The assumption made by Roser (Abstr., 1893, i, 177) that the hydroxydihydrobases of the pyridine and quinoline series are aldehyde bases, $R(NHMe)\cdot C\colon C\cdot CHO$, produced by ring-fission is unnecessary, because similar derivatives of the acridine group are known, and in this case the opening of the heterocyclic ring is not possible. These carbinol bases of the dihydroacridine series, however, behave in all respects precisely like the supposed aldehyde bases, and under the influence of alkalis undergo the characteristic transformation into methyldihydroacridine and methylacridone (Pictet and Patry, this vol., i, 644). The parallelism between the hydroxydihydro-bases of the pyridine and quinoline group on the one hand and hydrastinine and cotarnine on the other is maintained providing that the bases of both series are assumed to have the closed chain formula, with the reservation that in certain reactions they undergo an intermediate ring-fission. In accordance with this hypothesis, hydrastinine should have the carbinol constitution



$CH_2<\begin{matrix}O\cdot C\cdot CH\colon C\cdot CH_2\text{——}CH_2\\ O\cdot C\cdot CH\colon C\cdot CH(OH)\cdot NMe\end{matrix}$, whilst the papaveriniumalkylhydroxides of Goldschmiedt and Strausky should have formulæ corresponding with



$CH\lessgtr\begin{matrix}C_6H_2(OMe)_2\\ CH\text{——}NMe\end{matrix}>C<\begin{matrix}CH_2\cdot C_6H_3(OMe)_2\\ OH\end{matrix}$ (Abstr., 1888, 1116; 1889, 166; 1890, 179). Roser supposes that the isomeric change of ammonium base to carbinol derivative is due to the successive elimination and addition of water. This theory does not, however, account for the formation of carbinol ethers from the methiodides dissolved in absolute alcohol. The author is inclined to accept Hantzsch's ionisation theory, providing that it can be shown that the ionised part of the ammonium base undergoes only very slight isomerisation. The experimental evidence shows that the pyridinium and quinolinium hydroxides are comparatively stable in dilute aqueous solutions, and undergo isomeric change when these solutions are concentrated or when non-electrolytes are added. The alkali hydroxides produce a similar result, and these substances also tend to diminish the ionisation of the ammonium base. G. T. M.

Cinnamylquinine Hydrochloride. Kalle & Co. (D.R.-P. 131595).—*Cinnamylquinine hydrochloride*, $C_{29}H_{30}O_3N_2,HCl$, produced by adding cinnamyl chloride to quinine suspended in benzene, crystallises from hot water in white needles and melts at 235—236°.

Cinnamylquinine is set free by the action of sodium carbonate solution on the hydrochloride. G. T. M.

Action of Alcoholic Hydrogen Chloride on the Cerite Oxides. By Richard Jos. Meyer and M. Koss (*Ber.*, 1902, **35**, 2622—2626).—The very soluble chlorides of the cerite metals are readily obtained in a crystallised form by the use of alcoholic hydrogen chloride, and, moreover, the employment of this reagent permits of the isolation of double compounds of these chlorides with the organic amines. The pyridine derivatives are particularly characteristic, and their stability varies directly as the basic nature of the metallic radicle, the lanthanum double salt being most stable.

Strongly ignited didymium oxide dissolves in warm absolute alcohol saturated with hydrogen chloride, and the solution on cooling deposits the *alcoholate*, $DiCl_3,3EtOH$; this salt dissolves in alcoholic hydrogen chloride to a green solution, which, on treatment with pyridine, yields colourless needles of the pyridine double salt.

Black praseodymium peroxide dissolves only slowly in the solvent, the action being accompanied by reduction and the liberation of chlorine; the addition of pyridine to the solution leads to the formation of a double salt, $PrCl_3,3(C_5H_5N,HCl)$, crystallising with an indeterminate amount of alcohol.

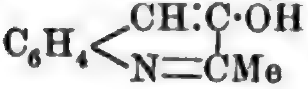
Neodymium oxide readily dissolves to a clear blue solution, and the *pyridine* salt, $NdCl_3,3(C_5H_5N,HCl)$, separating in blue needles, is more stable than the praseodymium derivative.

Alcoholic hydrogen chloride scarcely attacks cerium dioxide, but dissolves cerous carbonate, yielding a solution from which a sparingly soluble alcoholate separates; this compound rapidly loses alcohol on treatment with water, giving rise to the hydrated chloride $2CeCl_3,15H_2O$; the *pyridine* double salt, $CeCl_3,C_5H_5N,HCl,2EtOH$, separates in white, hygroscopic needles.

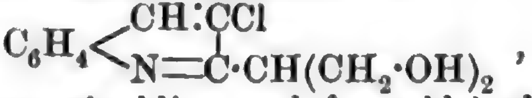
Lanthanum chloride, whether as hydrate or alcoholate, is very soluble in alcoholic hydrogen chloride, and consequently only concentrated solutions of the oxide yield the *chloride* $LaCl_3,2EtOH$; the *hydrated* salt, $2LaCl_3,15H_2O$, corresponds with the analogous cerous compound. The *pyridine* double salt, $2LaCl_3,3(C_5H_5N,HCl),2EtOH$ closely resembles the cerium derivative in outward appearance.

The *hydrated chlorides* of didymium and neodymium each contain $6H_2O$; the corresponding praseodymium salt crystallises with $7H_2O$.

G. T. M

β-Hydroxyquinaldine. Condensation of β-Chloroquinaldine with Formaldehyde. By Wilhelm Koenigs and Ferdinand Stockhausen (*Ber.*, 1902, 35, 2554—2562).—3-*Hydroxyquinaldine*,  $C_6H_4{<}\begin{matrix}CH{:}C\cdot OH\\ N{=}CMe\end{matrix}$, prepared from *o*-aminobenzaldehyde and chloroacetone, crystallises from hot dilute alcohol in glistening, pale yellow, odourless needles, becomes yellow at 240°, sinters and darkens at 250°, melts at 260° to a black liquid, and can be sublimed in small quantities in snow-white needles. The *platinichloride*, $(C_{10}H_9ON)_2,H_2PtCl_6,2H_2O$, forms glistening, orange-coloured needles or flakes, becomes dark, and melts with frothing at about 210°. The *hydrochloride* forms white, glistening, felted needles, begins to darken at 200°, sinters, becomes bluish-black, and finally melts to a black liquid at 265°. The *sulphate* crystallises from hot dilute sulphuric acid in beautiful, small needles containing water of crystallisation which is driven off at 140—145°, and melts at 192—193°. The *picrate* crystallises from alcohol in small, yellow, glistening needles, which darken, and then melt at 245—246° with vigorous frothing. The *ethyl ether* forms glistening, white, thin needles, which effloresce in air and sinter and melt at 69—70°.

3-*Chloro-2-αγ-dihydroxy*iso*propylquinoline*,



$$C_6H_4{<}\begin{matrix}CH{:}CCl\\ N{=}C\cdot CH(CH_2\cdot OH)_2\end{matrix},$$

prepared from 3-chloroquinaldine and formaldehyde, crystallises from hot water in long, white needles with a slightly yellow tint, which sinter and then melt at 122—123°; it melts under water to a yellowish oil, and yields formaldehyde when heated in a test-tube. The *platinichloride*, $(C_{12}H_{12}O_2NCl)_2,H_2PtCl_6,2H_2O$, forms small, red needles, sinters, blackens, and melts with frothing at 173°. The *aurichloride* forms golden-yellow, glistening, flat needles, sinters, and melts to a yellow liquid at 156°. The *picrate* forms beautiful, yellow needles, and sinters and melts at 147°. T. M. L.

Action of Alkyl Iodides on Tetrahydroquinolinecarboxylic Acids. By Otto Fischer and Rudolph Endres (*Ber.*, 1902, 35, 2611—2614. Compare Fischer, Abstr., 1899, i, 641).—The tetrahydroquinolinecarboxylic acids containing the carboxy-groups in the benzene nucleus behave towards methyl iodide precisely in the same way as tetrahydroquinoline-5-carboxylic acid, and give rise to the 1-methylcarboxylic acids, and not to methyl esters.

Tetrahydroquinoline-8-carboxylic acid is readily decomposed by boiling hydrochloric acid, and is therefore most readily produced by reducing quinoline-8-carboxylic acid with tin and hydrochloric acid at temperatures below 40—50°; its *nitrosoamine*, $C_{10}H_{10}ON_2$, crystallises in yellowish-white, hexagonal plates, and decomposes at 124°.

Kairoline-8-carboxylic acid, $C_{11}H_{13}O_2N$, obtained by digesting the potassium salt of the preceding acid with methyl iodide in methyl alcohol at 100°, crystallises from benzene in white needles and melts at 218—219°. 1-*Ethyltetrahydroquinoline-8-carboxylic acid*, produced in a similar manner by the action of alcoholic ethyl iodide, crystallises in white plates and melts at 196—197°.

Tetrahydroquinoline-7-carboxylic acid, prepared by reducing quinoline-*m*-carboxylic acid, crystallises from dilute alcohol in white leaflets melting at 189°; its ammonium salt gives white, yellowish-white, pink, and pale green, amorphous precipitates with silver, mercuric, ferric, and cupric salts respectively. Lead acetate gives a white, crystalline, insoluble lead salt, but calcium and barium chlorides do not produce precipitates. The *nitrosoamine* crystallises from benzene in yellowish-white needles and decomposes at 191°.

Kairoline-7-carboxylic acid and 1-*ethyltetrahydroquinoline-7-carboxylic acid*, the alkylation products of the preceding acid, separate from benzene in prismatic crystals melting respectively at 185° and 163—164°.

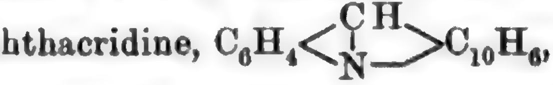
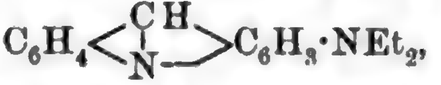
Tetrahydroquinoline-6-carboxylic acid is obtained by reducing quinoline-6-carboxylic acid, the latter being produced by oxidising 6-methylquinoline; it crystallises in white needles and decomposes at 170°, evolving carbon dioxide; the *nitrosoamine* forms yellowish-white prisms decomposing at 181°; the ammonium salt gives white, yellow, and grey precipitates with silver, lead, and cupric salts; the calcium and barium salts are soluble.

Kairoline-6-carboxylic acid, prepared like the methylcarboxy-acids, crystallises from benzene in four-sided prisms melting and decomposing at 224°.

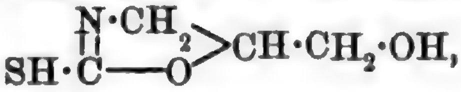
1-*Ethyltetrahydroquinoline-6 carboxylic acid* crystallises from benzene in leaflets and melts at 200° to a red oil.

In all these cases, the products of alkylation are completely soluble in cold dilute solutions of the alkali hydroxides, and hence no alkyl esters are formed.

The alkylated carboxy-acids melt at higher temperatures than the corresponding tetrahydroquinolinecarboxylic acids. G. T. M.

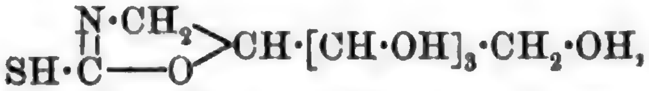
Acridine Syntheses by Means of *o*-Aminobenzyl Alcohol. By FRITZ ULLMANN and C. BAEZNER (*Ber.*, 1902, **35**, 2670—2672).—1:2-Phenonaphthacridine,  $C_6H_4\left<\begin{matrix}CH\\|\\N\end{matrix}\right>C_{10}H_6$, is prepared by heating together *o*-aminobenzyl alcohol and β-naphthol finally at 200—210°; the substance is isolated in the form of the picrate. It forms pale yellow crystals melting at 131°, and is identical with the compound obtained from formaldehyde, aniline, and β-naphthol; it can also be prepared by melting together *o*-aminobenzyl alcohol and β-naphthylamine, or from *o*-aminobenzyl sulphide and β-naphthol. 3-Diethylaminoacridine,  $C_6H_4\left<\begin{matrix}CH\\|\\N\end{matrix}\right>C_6H_3\cdot NEt_2$, is prepared by heating *o*-aminobenzyl alcohol and diethyl-*m*-aminophenol in carbon dioxide at 210°; the picrate crystallises in orange needles; the solutions of the base are yellow in colour and have a green fluorescence.

K. J. P. O.

Action of Carbon Disulphide on Polyhydric Aminoalcohols. By LÉON MAQUENNE and E. ROUX (*Compt. rend.*, 1902, **134**, 1589—1592).—Polyhydric aminoalcohols react with carbon disulphide in a manner differing from that of monohydric aminoalcohols (Gabriel, Abstr., 1889, 870, and 1890, 472). When aminopropyleneglycol in aqueous solution is heated at 100° with carbon disulphide, *mercaptomethyloloxazoline*,  $\begin{array}{l}\mathrm{N\cdot CH_2} \\ \;\| \\ \mathrm{SH\cdot C{-}{-}O}\end{array}\!\!>\mathrm{CH\cdot CH_2\cdot OH}$, is formed; it is purified by adding silver nitrate to its aqueous solution, when an almost insoluble *silver* derivative, $C_4H_6O_2N\cdot SAg,HNO_3$, is precipitated; the latter crystallises in small, colourless plates; excess of silver nitrate produces a *di-silver* derivative, $C_4H_6O_2N\cdot SAg,AgNO_3$, which crystallises in slender needles, and is converted by nitric acid into the mono-silver derivative. From the latter, ammonia sets free the base,

$$C_4H_6O_2N\cdot SAg,$$

which is gelatinous, and converted by hydrogen sulphide into the oxazoline; this substance is a colourless, syrupy oil, very soluble in water, is without taste or smell, and is not attacked by alkalis or concentrated acids.

Mercaptobutyltetroloxazoline,  $\begin{array}{l}\mathrm{N\cdot CH_2} \\ \;\| \\ \mathrm{SH\cdot C{-}{-}O}\end{array}\!\!>\mathrm{CH\cdot [CH\cdot OH]_3\cdot CH_2\cdot OH}$, prepared from glucamine and carbon disulphide at 100°, crystallises in needles melting at 156°; its *di-silver* derivative,

$$C_7H_{12}O_5N\cdot SAg,AgNO_3,$$

is formed as a white, crystalline precipitate when silver nitrate is added to its aqueous solution; nitric acid dissolves it, but does not convert it into the mono-silver derivative; the base is obtained as a gelatinous precipitate on treating the silver derivative with ammonia.

K. J. P. O.

Thiopyronine. By JOACHIM BIEHRINGER and WASSIL TOPALOFF (*J. pr. Chem.*, 1902, [ii], **65**, 499—511. Compare Abstr., 1897, i, 73).—On treatment of tetramethyldiaminodiphenylmethane with a solution of sulphur in sulphuric acid containing 25 per cent. of sulphur trioxide, dilution with water and addition of zinc chloride, *thiopyronine zinc chloride* crystallises out in red-green, glistening leaflets, which dissolve in water to a red solution with yellow fluorescence; the mother liquor contains unchanged tetramethyldiaminodiphenylmethane along with the corresponding benzhydrol.

On addition of sodium hydroxide to the aqueous solution of the double salt, the *thiopyronine* forms a violet, flocculent precipitate which contains more or less *tetramethyldiaminothioxanthone*. The thiopyronine is soluble in warm alcohol, acetone, or chloroform, more sparingly in hot benzene to red solutions with weak yellow fluorescence. On addition of sodium hydroxide to the alcoholic solution, the red colour disappears and is replaced by the blue fluorescence of the thioxanthone. Thiopyronine forms a *hydrochloride*, $C_{17}H_{18}N_2S,2HCl$, crystallising in golden-green, glistening needles which melt at 245°, and a *platinichloride*, $(C_{17}H_{18}N_2S)_2,H_2PtCl_6$, crystallising in glistening, green needles. The *leuco*-base, formed by reduction with zinc dust and hydrochloric acid, crystallises from dilute alcohol in clusters of colourless needles, melts at 130°, and is easily oxidised to the dye.

Tetramethyldiaminothioxanthone, formed by oxidation of thiopyronine by potassium permanganate in aqueous potassium hydroxide solution, or by warming with aqueous sodium hydroxide, crystallises in yellow prisms, melts at 288°, when heated is partially volatile without decomposition, and is easily soluble in hot chloroform, but only sparingly so in hot ethyl acetate, petroleum, benzene, or acetone. The solution in petroleum is colourless, in other solvents yellow; the alcoholic and acetone solutions have a distinct blue fluorescence, the solution in concentrated sulphuric acid has a strong green fluorescence which changes to blue on addition of much alcohol and disappears on addition of water.

The *hydrochloride*, $C_{17}H_{18}ON_2S,2HCl,3\frac{1}{2}H_2O$, is a stellate, crystalline, reddish-yellow mass, which loses water and hydrogen chloride on warming. The *platinichloride*, $(C_{17}H_{18}ON_2S)_2,H_2PtCl_6$, forms clusters of yellow needles.

The hydrobromide of the *tribromo*-derivative, $C_{17}H_{15}ON_2SBr_3,HBr$, formed by the action of bromine in boiling glacial acetic acid solution, crystallises in plates and melts and decomposes at 235°. The tribromo-derivative, precipitated by ammonia from its solution in acetic acid, crystallises from acetone in red leaflets. G. Y.

Thiosemicarbazide as a Reagent for Aldehydes and Ketones.

By Martin Freund and Alfred Schander (*Ber.*, 1902, **35**, 2602—2606. Compare Neuberg and Neimann, this vol., i, 572, and Abstr., 1897, i, 125, 126).—The following thiosemicarbazones were prepared to illustrate the employment of thiosemicarbazide in the identification and characterisation of aldehydes and ketones; they are obtained by mixing their generators either alone or in acetic acid, alcoholic, or aqueous solutions.

Acetaldehydethiosemicarbazone, $CHMe\!:\!N\cdot NH\cdot CS\cdot NH_2$, separates from water in white crystals and melts at 146°.

Citraldehydethiosemicarbazone forms white flakes and melts at 107—108°.

Benzaldehydethiosemicarbazone, $CHPh\!:\!N\cdot NH\cdot CS\cdot NH_2$, a yellowish-white, crystalline product, sinters at 155° and melts at 160°.

Salicylaldehydethiosemicarbazone forms yellow crystals, sinters at 215°, and melts at 231°.

p-*Hydroxybenzaldehydethiosemicarbazone* separates from methyl or ethyl alcohol in slender, felted, yellow needles, sintering at 215° and melting at 224°.

Cinnamaldehydethiosemicarbazone, a white, crystalline substance, melts at 123°. *Vanillinthiosemicarbazone* separates in slender, yellow needles, sintering at 194° and melting at 196—197°.

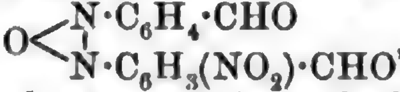
Acetonethiosemicarbazone, $CMe_2\!:\!N\cdot NH\cdot CS\cdot NH_2$, is a white, crystalline compound sintering at 174° and melting at 179°.

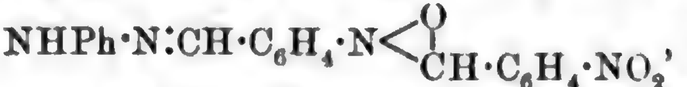
Ethyl acetoacetate-thiosemicarbazone, $C_6H_{10}O_2\!:\!N\cdot NH\cdot CS\cdot NH_2$, separates from hot water as an oil which solidifies to a white, crystalline mass; it melts at 97°.

Ethyl succinylsuccinate-bisthiosemicarbazone is a yellow, crystalline mass insoluble in all the ordinary solvents; it turns brown at 250°, but does not melt below 275°.

Diketohexamethylenebisthiosemicarbazone, $C_6H_8(\!:\!N\cdot NH\cdot CS\cdot NH_2)_2$, is an insoluble, white, crystalline mass which darkens and melts at 210—215°. G. T. M.

p-**Azoxybenzaldehyde.** By **Friedrich J. Alway** (*Amer. Chem. J.*, 1902, **28**, 34—48).—It has been shown by Gattermann (Abstr., 1897, i, 189) that when *p*-nitrobenzaldehyde is submitted to electrolytic reduction, the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime is produced. If this substance is treated with ferric chloride, a compound is obtained identical with the *p*-azoxybenzaldehyde described by Kirpal (Abstr., 1897, i, 520).

p-Azoxybenzaldehyde melts at 190° (not at 194° as stated by Kirpal); it undergoes no change when treated with concentrated sulphuric acid at 100°, and is not affected by concentrated nitric acid, benzoyl chloride, acetyl chloride, or nitrous acid. By the action of zinc dust and acetic acid on the aldehyde, a red, crystalline substance is produced. The phenylhydrazone melts at 228°. p-*Azoxybenzylideneaniline*, $ON_2(C_6H_4\cdot CH{:}NPh)_2$, obtained by boiling the aldehyde with excess of aniline, crystallises in large, yellow leaflets and melts at 185—192°. The *nitro*-derivative,  $O<\begin{matrix}N\cdot C_6H_4\cdot CHO\\ | \\ N\cdot C_6H_3(NO_2)\cdot CHO\end{matrix}$, prepared by treating the aldehyde with hot fuming nitric acid, forms yellow needles, melts at 171—172°, and is readily soluble in hot acetic acid. p-*Azoxybenzylidene chloride*, $ON_2(C_6H_4\cdot CHCl_2)_2$, obtained by the action of phosphorus pentachloride on the aldehyde, crystallises in orange-coloured leaflets and melts at 115—116°.

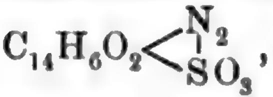
The *phenylhydrazone* of the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime,  $NHPh\cdot N{:}CH\cdot C_6H_4\cdot N<\begin{matrix}O\\ | \\ CH\cdot C_6H_4\cdot NO_2\end{matrix}$, forms dark red leaflets and melts at 222°. When the N-*p*-formylphenyl ether of *p*-nitrobenzaldoxime is heated with aniline, the *anilide* of p-*aldehydohydrazobenzene*, $NHPh\cdot NH\cdot C_6H_4\cdot CH{:}NPh$, is produced, which crystallises in orange-coloured leaflets and melts at 183—186°.

If *p*-nitrosobenzaldehyde is added to concentrated sulphuric acid, a *substance*, $(C_7H_5O_2N)_x$, is obtained, which forms a dark red powder and melts at 204—206°. By the action of aniline on *p*-nitrosobenzaldehyde, *benzeneazobenzylideneaniline*, $PhN{:}N\cdot C_6H_4\cdot CH{:}NPh$, is produced, which crystallises in small, orange-coloured needles and melts at 125—130°; if this compound is treated with boiling dilute acetic acid, *benzeneazobenzaldehyde*, $C_6H_5\cdot N{:}N\cdot C_6H_4\cdot CHO$, is formed, which crystallises in lustrous, brownish-red leaflets and melts at 116°. The *phenylhydrazone* of benzeneazobenzaldehyde forms long, red needles and melts at 154°.

The *aldehyde*, obtained from *m*-nitrobenzaldehyde by methods analogous to those used in the conversion of *p*-nitrobenzaldehyde into *p*-azoxybenzaldehyde, melts at 129° and yields a *phenylhydrazone* melting at 198°. E. G.

Dibenzoylhydrazobenzene. By **Paul Freundler** (*Compt. rend.*, 1902, **134**, 1509—1510).—Biehringer and Busch (this vol., i, 575) have described dibenzoylhydrazobenzene as a substance melting at 161°, which, when saponified, gives aniline. *Dibenzoylhydrazobenzene* has been prepared by a method different from that employed by the authors mentioned, but it melts at 138° and is easily saponified with dilute alkali, giving hydrazobenzene.

The compound described by Biehringer and Busch has been identified as benzaniline. J. McC.

Replacement of the Diazo-group by Amidogen. By LEONHARD WACKER (*Ber.*, 1902, **35**, 2593—2602).—The *anhydride*,  $C_{14}H_6O_2{<}\begin{matrix}N_2\\ |\\ SO_3\end{matrix}$, of 1-diazoanthraquinone-2-sulphonic acid, obtained by treating 1-aminoanthraquinone-2-sulphonic acid, or 1-hydroxylaminoanthraquinone-2-sulphonic acid, with nitrous acid, is a light yellow, crystalline powder decomposing at 142°. When suspended in water and treated with ammonia or ammonium carbonate, this diazo-compound is reconverted into the original aminosulphonic acid, the reaction being accompanied by an elimination of nitrogen. Other primary amines produce a similar effect, but give rise, in the first place, to intermediate diazoamines. Aniline and the diazoanhydride yield a diazoamino-compound which is isolated in the form of its *potassium* salt, $NHPh{\cdot}N_2{\cdot}C_{14}H_6O_2{\cdot}SO_3K$, a voluminous, orange-yellow precipitate, which, when boiled with dilute sulphuric acid, evolves nitrogen and becomes decomposed into phenol and the original aminosulphonic acid.

A red diazoamino-compound is formed from the diazoanhydride and methylamine; it is readily decomposed by warm water or dilute acids, also giving rise to the original aminosulphonic acid. These reactions are assumed to be due to the following series of changes, $NHR{\cdot}N_2{\cdot}C_{10}H_6O_2{\cdot}SO_3H \rightarrow R{\cdot}N_2{\cdot}NH{\cdot}C_{10}H_6O_2{\cdot}SO_3H \rightarrow R{\cdot}OH + N_2 + NH_2{\cdot}C_{10}H_6O_2{\cdot}SO_3H$. This assumption is justified by the fact that diethylamine and the diazoanhydride combine to form a diazoamino-compound, which, when heated with dilute acid, decomposes into diethylamine, 1-hydroxyanthraquinone-2-sulphonic acid, and nitrogen. In this case, the initial rearrangement of the diazoamino-compound is not possible.

When hydroxylamine hydrochloride and the diazoanhydride are condensed in the presence of sodium acetate, a *diazohydroxyamide*, $OH{\cdot}NH{\cdot}N_2{\cdot}C_{10}H_6O_2{\cdot}SO_3Na$, is produced as a yellowish-brown, amorphous product, which, when warmed with concentrated sulphuric acid at 70°, becomes transformed quantitatively into 1-amino-4-hydroxyanthraquinone-2-sulphonic acid. The potassium salt of the latter acid dissolves in water to a red solution; the acid itself can be diazotised and condensed with hydroxylamine, the product dissolving in water to a pink solution which changes to a greenish-blue colour when rendered alkaline. This reaction serves to identify the aminohydroxy-acid. Hydrazine and the diazoanhydride condense to form a diazohydrazide; this substance, when treated with cold concentrated sulphuric acid, furnishes a good yield of 1-amino-2-hydroxyanthraquinone-2-sulphonic acid; this result involves the following changes:

$$NH_2{\cdot}NH{\cdot}N_2{\cdot}C_{10}H_6O_2{\cdot}SO_3H \rightarrow NH_2{\cdot}N_2{\cdot}NH{\cdot}C_{10}H_6O_2{\cdot}SO_3H + H_2O \rightarrow N_2 + NH_3 + NH_2{\cdot}C_{10}H_5(OH)O_2{\cdot}SO_3H.$$

The aminohydroxy-acid was also identified by conversion into a quinizarin-green-sulphonic acid by heating with boric acid, stannous chloride, and *p*-toluidine. G. T. M.

Action of Diazo-salts on Desmotroposantonin and Desmotroposantonous Acid. By EDGAR WEDEKIND and OSCAR SCHMIDT (*Compt. rend.*, 1902, **135**, 43—45).—Santonin does not combine with diazo-salts, but desmotroposantonin combines readily with the diazo-salts of *p*-toluidine, *o*-nitroaniline, *p*-nitroaniline, *p*-aminobenzoic acid, sulphanilic acid, and tolidine, yielding yellow or red crystallisable compounds which melt above 260°.

Desmotroposantonous acid similarly combines with the diazo-derivatives of aniline and *p*-toluidine, forming compounds which melt about 50° lower than the corresponding compounds from desmotroposantonin.

The different behaviour of santonin and desmotroposantonin towards diazo-compounds agrees with Andreocci's view as to their constitution (Abstr., 1894, i, 205). C. H. B.

New Amino-acid from Gelatin. By EMIL FISCHER (*Ber.*, 1902, **35**, 2660—2665).—Hydroxyamino-acids are present in the hydrolytic products of proteids, gelatin, &c. A new hydroxyamino-acid can be isolated from the mother liquor from which the esters of the monoamino-acids have been extracted (see this vol., i, 512) in the hydrolysis of gelatin. The thick mother liquor is dissolved in water, acidified, and slowly evaporated; during the evaporation, the inorganic salts partly separate; the syrupy mother liquor is repeatedly treated with alcoholic hydrogen chloride and evaporated in vacuum to remove monoamino-acids. The residue, which consists only of salts, diamino-acids, and hydroxyamino-acids is dissolved in water, saturated with hydrogen chloride, evaporated, and treated with alcoholic hydrogen choride; the inorganic salts are thus completely removed. From the aqueous solution of the residue, the hydroxyamino-acid can be precipitated by phosphotungstic acid. From 1 kilogram of gelatin, 30 grams of crude crystallised product were obtained. The *acid*, $C_5H_9O_3N$, crystallises in colourless plates belonging to the rhombic system $[a : b : c = 0{\cdot}59405 : 1 : 0{\cdot}3579]$, and has $[\alpha]_D - 81{\cdot}04°$ at 20°; when heated, the acid decomposes at 270°, and gives off vapour containing pyrrole. The *copper* salt forms deep blue, very soluble crystals. With phenylcarbimide, it forms a *compound*, $C_{12}H_{14}O_4N_2$, which crystallises in colourless leaflets melting and decomposing at 175°. On reducing the hydroxyamino-acid with phosphorus and hydriodic acid, *r*-2-pyrrolidinecarboxylic acid is obtained. The new acid is therefore a hydroxypyrrolidine-2-carboxylic acid.

A description is given of the taste of the various classes of amino-acids. K. J. P. O.

Basic Products of the Profound Hydrolysis of Muscle. By ALEXANDRE ÉTARD (*Bull. Soc. Chim.*, 1902, [iii], **27**, 693—696).—From calf's muscle macerated in sulphuric acid and heated with this in a reflux apparatus, the author obtained leucine, tyrosine, glycine, and glutamic acid. Other basic substances, for example, one similar to lysine carbonate, have been obtained, but not in a condition suitable for analysis. A. F.

Certain Chemical and Physical Properties of Hæmoglobin. By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1902, **70**, 79—83).—Solutions containing oxyhæmoglobin of great purity and in varying concentration were prepared, and photographs of the cadmium spark spectrum, with and without the interposition of the solutions, were obtained. There are no absorption bands corresponding with either the 14th or 17th cadmium line, and the band observed by Soret corresponding with the 14th is therefore due, not to the blood colouring matter, but to some other constituent.

The author's investigations show that the conductivity of oxyhæmoglobin solutions is low, but very much higher than that found by Stewart at 5°. The conductivity increases rapidly with rising temperature, and undergoes permanent changes when the solutions are kept for even a short time above 0°.

When oxyhæmoglobin solutions are electrolysed, the anode and cathode being separated by an animal membrane, there is first of all a separation of colloidal hæmoglobin in the anode compartment, and then a rapid and complete transport of the same to the cathode compartment. The author considers this process to be of a similar nature to the phenomena of electro-endosmose, studied by Quincke. What has been said with regard to oxyhæmoglobin applies also to carbon monoxide hæmoglobin.

Evidence is brought forward to prove that the precipitated colloidal, and yet perfectly soluble, hæmoglobin represents the undecomposed molecule of the blood colouring matter. The readiness with which this colloidal hæmoglobin passes through animal membranes under the conditions just mentioned suggests that certain absorption phenomena in the animal body may be intimately connected with electromotive changes in the tissues. J. C. P.

Action of Phosphorus Pentachloride on Aniline. By J. ELLIOTT GILPIN (*Amer. Chem. J.*, 1902, **27**, 444—454. Compare Abstr., 1897, i, 463).—When a cold saturated solution of phosphorus pentachloride in benzene is added slowly to a benzene solution of aniline and the mixture left for some time, aniline hydrochloride separates. When the benzene is distilled off and the residue washed with boiling water and crystallised from hot alcohol, the compound, $P(NPh)_2\cdot NHPh$, separates in well-defined, rhombic crystals [$a:b:c$: 0·27956 : 1 : 0·258614], which melt at 208—210°. The substance is not acted on by water or alcoholic potassium hydroxide, but is decomposed by concentrated sulphuric acid or concentrated nitric acid.

When aniline acts on phosphorus pentachloride at a high temperature the compound, $P_2Cl(NHPh)_7$, is formed as a bye-product, and is extracted from the mixture by means of a small quantity of alcohol. It crystallises with 2 mols. of alcohol in monoclinic crystals [$a:b:c$: 1·32375 : 1 : 0·55845], and exhibits a hemihedral habit. It melts at 192—194°. J. McC.

Organic Chemistry.

Direct Hydrogenation of Acetylene Hydrocarbons by Contact Action. By Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1902, **135**, 87—89).—Heptylidene, in presence of excess of hydrogen and in contact with reduced nickel at about 170°, is converted into normal heptane together with small quantities of higher hydrocarbons of the same series. Reduced copper above 200° produces α-heptylene, diheptylene, and triheptylene as well as normal heptane. Phenylacetylene, in presence of excess of hydrogen, is converted by nickel at about 180° into ethyl*cyclo*hexane boiling at 130° together with a small quantity of methyl*cyclo*hexane. Copper at 190° to 250° converts the phenylacetylene mainly into metastyrene, ethylbenzene, and diphenylbutane, the yield of the last reaching as much as 50 per cent. (compare this vol., i, 525). C. H. B.

Reduction of Nitro-compounds by Direct Hydrogenation in Contact with Finely Divided Metals. By Paul Sabatier and Jean B. Senderens (*Compt. rend.*, 1902, **135**, 225—227. Compare Abstr., 1901, i, 459).—α-Nitronaphthalene with an excess of hydrogen, when in contact with finely divided copper at 330—350°, is reduced to α-naphthylamine. The reduction can also be carried out with a mixture of carbon monoxide and hydrogen. With nickel at the same temperature, the reduction proceeds further, so that some tetrahydronaphthalene is produced.

In presence of reduced nickel at 150—180°, nitromethane is completely reduced to methylamine, but at 320° reduction takes place to methane and ammonia. Nitromethane is not reduced by hydrogen in presence of copper below 300°; above this temperature, reaction takes place, part of the nitromethane suffers reduction, and a compound of nitromethane with methylamine results, the product being identical with a solution of nitromethane in aqueous methylamine.

With nickel at 200°, nitroethane is easily reduced to ethylamine. The reaction with copper is analogous to that found for nitromethane. J. McC.

Action of Hydrazine Hydrate on the Aldol from *iso*Butyraldehyde and Formaldehyde. By Berthold König (*Monatsh.*, 1902, **23**, 469—478. Compare Abstr., 1900, i, 212, 428).—*γ-Hydroxy-ββ-dimethylpropionaldazine*, $(OH\cdot CH_2\cdot CMe_2\cdot CH{:})_2N_2$, formed by the action of hydrazine hydrate on the aldol obtained from *iso*butyraldehyde and formaldehyde, crystallises in colourless masses, melts at 151°, boils and decomposes at 190° under atmospheric pressure, at 165° under 25 mm. pressure, is easily soluble in acetone, alcohol, ether, benzene, chloroform, or water, but only sparingly so in carbon disulphide or light petroleum, and gives the pyrazoline reactions with potassium permanganate or with wood-fibre in dilute hydrochloric acid (Abstr., 1895, i, 248).

Cryoscopic and ebullioscopic molecular weight determinations indicate the formula $C_{10}H_{20}O_2N_2$. When distilled or when exposed to moist air containing acid vapours, the aldazine is decomposed, giving an odour of amines and of ammonia.

When heated with dilute sulphuric acid at 90°, boiled with dilute aqueous or alcoholic hydrochloric acid, or when treated with hydrogen chloride in benzene solution, the aldazine is hydrolysed to hydrazine and the aldol.

When heated with maleic acid at 130°, the aldazine forms a yellow, crystalline *derivative* which melts at 121°, decomposes at 150°, and is probably a pyrazoline compound. G. Y.

Sulphur and Nitrogen Derivatives of Carbon Disulphide. V. Dithiocarbamic Esters derived from Secondary Aromatic Amines. VI. Aromatic Iminodithiocarbonic Esters. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1902, [iii], 27, 807—812. Compare Abstr., 1901, i, 518; this vol., i, 199, 353, 595, 597).—By the action of carbon disulphide on methylaniline in presence of an alcoholic solution of ammonia, the author obtained *ammonium methylphenyldithiocarbamate*, $NMePh{\cdot}CS{\cdot}SNH_4$, in the form of yellowish, lozenge-shaped plates, sparingly soluble in cold water or alcohol, and insoluble in ether; it is only slightly stable in air. *Ammonium phenylethyldithiocarbamate*, obtained in a similar manner, is closely analogous in its properties to the preceding compound. Dithiocarbamic esters can be readily prepared by acting with an alkyl haloid on the preceding salts suspended in cold alcohol.

By acting on a dithiocarbamic ester derived from aniline in cold ethereal solution with methyl iodide, the hydriodide of an iminodithiocarbonic ester is obtained which decomposes in aqueous solution into the ester and hydriodic acid. On employing an alcoholic solution and heating at 50—70°, the ester is also formed, but the reaction is more complicated. Quantitative yields are obtained by acting with an alkyl iodide on dithiocarbamates dissolved in alcoholic solutions of potassium hydroxide. *Methyl phenyliminodithiocarbonate*, $NPh{:}C(SMe)_2$, boils at 300°, solidifies on cooling, and crystallises from alcohol in elongated prisms which melt at 36°. The *hydriodide* melts between 110° and 120° and froths at about 130°. The *picrate* is viscous and is decomposed by water. *Methyl* p-*tolyliminodithiocarbonate*, $C_6H_4Me{\cdot}N{:}C(SMe)_2$, boils at 315°. A. F.

Sulphur and Nitrogen Derivatives of Carbon Disulphide. VII. Dithiocarbamic Esters derived from Primary Amines. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1902, [iii], 27, 812—818. Compare preceding abstract).—These are best prepared by acting on the sulphocarbonic derivatives of primary amines with 1 mol. of an alkyl haloid. In this way, the author has prepared *methyl methyldithiocarbamate*, $NHMe{\cdot}CS{\cdot}SMe$, a thick, heavy, refractive liquid which crystallises in methyl chloride; *ethyl methyldithiocarbamate*, an oily liquid; *benzyl methyldithiocarbamate*, which crystallises in small plates melting at 49·5°; and benzyl phenyldithiocarbamate.

On being heated, these compounds all decompose into thiocarbimide and mercaptan. When heated with ammonia or with amines, they also undergo decomposition with formation of substituted thiocarbamides and mercaptan, a reaction which constitutes a new method of synthesis of mono-, di-, *s*-, and tri-substituted thiocarbamides. The dithiocarbamic esters derived from primary amines also combine with a second mol. of an alkyl haloid, yielding symmetrical or mixed iminodithiocarbonic esters. When subjected to the action of ferric chloride, those dithiocarbamates in which a fatty radicle is attached to nitrogen are unattacked, whilst those in which an aromatic radicle is attached to nitrogen give rise to *isothiuram disulphides*; the *compound* $NPh\colon C(SMe)\cdot S\cdot S(SMe)\cdot C\colon NPh$ forms colourless needles melting at 123°, and the *compound*

$$C_6H_4Me\cdot N\colon C(SMe)\cdot S\cdot S(SMe)\cdot C\colon N\cdot C_6H_4Me\ [Me:N=1:4]$$

forms colourless needles melting at 158°.

To explain the difference in the behaviour of the primary dithiocarbamates, the author, as also for other reasons, considers that the two classes of compounds differ in constitution, those derived from fatty amines having their hydrogen attached to nitrogen, whereas in the compounds derived from aromatic amines, the hydrogen is attached to sulphur. A. F.

Action of Organic Acids on Metallic Antimony. I. By B. Moritz and C. Schneider (*Zeit. physikal. Chem.*, 1902, **41**, 129—138).—When powdered antimony is shaken with solutions of certain organic acids in the presence of air, the antimony is attacked. The presence of air is essential, and the diminution of the air volume accompanying the action corresponds with the quantity of oxygen it contains and with the quantity of antimony which has passed into solution. Only acids containing the hydroxyl as well as the carboxyl group have the power of attacking antimony under the above conditions; further, it appears that the hydroxyl and carboxyl groups must be attached to the same carbon atom; thus, whilst α-hydroxybutyric acid acts readily on the metal, the β-acid is almost without effect. In all cases, the quantity of antimony passing into solution is greatest when the acid has been partly neutralised with soda, and the mixture therefore contains the acid salt. Of dibasic acids, oxalic, malic, tartaric, and citric acids readily attack antimony as above described. Malonic and succinic acids, on the other hand, are without effect, and the same holds for phenol and benzoic and salicylic acids. Solutions of gallic and tannic acids produce in a few minutes precipitates containing antimony.

In the course of their work, the authors have isolated a crystalline compound of lactic acid with sodium and antimony, having the empirical formula $SbONa_2(C_3H_5O_3)_3$. J. C. P.

Mercury Lactates. By Marcel Guerbet (*Bull. Soc. Chim.*, 1902, [iii], **27**, 803—807).—The author has prepared mercurous lactate by dissolving freshly precipitated mercurous oxide in dilute lactic acid, previously heated with water in order to destroy the anhydride, &c., which it contains. The solution thus obtained is allowed to evaporate in a desiccator over sulphuric acid, when mercurous lactate separates out in short, white, prismatic needles having the composition $(C_3H_5O_3)_2Hg_2,H_2O$. It does not dissolve entirely in water, hydrolysis occurring with formation of a basic lactate, which then decomposes into mercuric lactate and mercury.

In a similar manner, by dissolving yellow mercuric oxide in dilute lactic acid and allowing the solution to evaporate over sulphuric acid, mercuric lactate separates out in colourless prismatic needles having the composition $(C_3H_5O_3)_2Hg$. It is very soluble in water; on boiling this solution, the mercuric salt passes into mercurous, and there are formed at the same time carbon dioxide, aldehyde, and lactic acid.

The substances described as lactates of mercury by Engelhard and Maddrel and by Brüning are found by the author to be mixtures.

A. F.

Action of Nitrous Acid on α-Substituted β-Ketonic Esters. Synthesis of the Homologues of Pyruvic Acid. By LOUIS BOUVEAULT and RENÉ LOCQUIN (*Compt. rend.*, 1902, **135**, 179—182).—By the action of nitrous acid on α-substituted acetoacetates, two products are formed according to the equations: (I) $COMe\cdot CHR\cdot CO_2Et + HNO_2 = Me\cdot CO_2H + NOH\colon CR\cdot CO_2Et$ and (II) $COMe\cdot CHR\cdot CO_2Et + HNO_2 = EtOH + COMe\cdot CR\colon NOH + CO_2$. In acid solution, the former reaction takes place exclusively. The same oximoglyoxylic ester is obtained in starting with ethyl ethylhexoylacetate or ethyl ethylacetoacetate, namely, $NOH\colon CEt\cdot CO_2Et$. This *oxime* of *ethyl methylpyruvate* boils at 125—130° under 10 mm. pressure; it crystallises in white needles which are soluble in light petroleum and melt at 58°. From ethyl *iso*amylacetylacetate, the authors have prepared the *oxime* of *ethyl* iso*butylpyruvate*, $CHMe_2\cdot[CH_2]_2\cdot C(\colon NOH)\cdot CO_2Et$, as an oil which boils at 114° under 12 mm. pressure and has a sp. gr. 0·9114 at 4°/0°. The corresponding acid, obtained by saponification, melts at 160° with decomposition. *Ethyl* iso*butylpyruvate* boils at 105° under 18 mm. pressure. Starting with ethyl *sec.*octylacetoacetate, the *oxime* of *ethyl methylhexylpyruvate*, $CH_2Me\cdot[CH_2]_4\cdot CHMe\cdot C(\colon NOH)\cdot CO_2Et$, has been obtained as an oil which boils at 177° under 16 mm. pressure and has a sp. gr. 0·9859 at 4°/0°. The corresponding acid melts at 88—89°.

J. McC.

Preparation of α-Derivatives of β-Ketonic Esters. By RENÉ LOCQUIN (*Compt. rend.*, 1902, **135**, 108—110).—When the C-esters of the acylacetoacetates (Abstr., 1901, i, 311) are treated with an alkyl iodide and a sodium alkyloxide in presence of an excess of alcohol, a good yield is obtained in accordance with the equation

$$CHAc(COR)\cdot CO_2Et + NaOEt + R'I = Me\cdot CO_2Et + NaI + R\cdot CO\cdot CHR'\cdot CO_2Et,$$

whilst if an alkyl bromide is used the reaction is more complicated and proceeds partly in accordance with the equation

$$CHAc(COR)\cdot CO_2Et + NaOEt + R'Br = R\cdot CO_2Et + NaBr + CHAcR'\cdot CO_2Et.$$

Ethyl ethylhexoylacetate, boiling at 128—129° under 13 mm. pressure, and of sp. gr. 0·9325 at 4°/0°, is obtained in this way from *ethyl C-hexoylacetoacetate*, which boils at 136° under 10 mm. pressure and has a sp. gr. 1·032 at 0°. The corresponding *4-ethyl-3-amyl pyrazolone* melts at 136°. The action of ethyl bromide on ethyl C-butyrylacetoacetate yields a mixture of ethyl ethylacetoacetate and *ethyl ethyl-*

butyrylacetate which cannot be separated by fractionation, but 3-*methyl*-4-*ethyl pyrazolone* corresponding with the former melts at 190°, whilst 4-*ethyl*-3-*propylpyrazolone* corresponding with the latter melts at 145° and is more soluble in alcohol or ether. *Ethyl hexylbutyrylacetate*, $CH_2Me\cdot CH_2\cdot CO\cdot CH(CHMe\cdot [CH_2]_5\cdot Me)\cdot CO_2Et$, obtained by the action of secondary octyl iodide on ethyl C-butyrylacetoacetate, boils at 166° under 16 mm. pressure and has a sp. gr. 0·9347 at 4°/0°. Its pyrazolone is liquid and boils and partially decomposes at about 270° under 30 mm. pressure. C. H. B.

Di-*p*-phenetidide of Agaric Acid. J. D. Riedel (D.R.-P. 130073).—The *di*-p-*phenetidide* of agaric acid, produced by heating this acid with 2·5 mols. of *p*-phenetidine at 140—160° either under pressure or in a current of indifferent gas, crystallises from glacial acetic acid, alcohol, or a mixture of benzene and petroleum in small needles melting at 150—151°; it is insoluble in water or dilute acid or alkaline solutions. The compound is very soluble in cold chloroform, but dissolves less readily in other organic solvents of low boiling point.

G. T. M.

Action of Alkali Nitrites on *a*-Substituted *β*-Ketonic Esters. By Louis Bouveault and René Locquin (*Compt. rend.*, 1902, 135, 295—297).—When ethyl *iso*amylacetoacetate is treated successively with an alkali hydroxide, sodium nitrite, and an acid, it yields, in almost calculated quantity, *nitroso*iso*amylacetone*,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CAc\colon NOH,$$

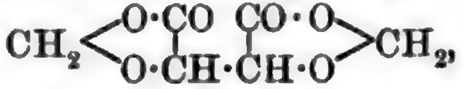
which melts at 32—33°, boils at 128° under 18 mm. pressure and with hydroxylamine yields a dioxime melting at 181°. With the higher homologues of the ester, however, the reaction does not succeed, because the action of the alkali hydroxide yields a very unstable salt, which decomposes in accordance with the equation

$$R\cdot CO\cdot CHR'\cdot CO_2Na + NaOH = R\cdot CO\cdot CH_2R' + Na_2CO_3.$$

If, however, the ester is mixed with the calculated quantity of sodium ethoxide in presence of absolute alcohol and dry ethyl nitrite is passed into the solution, the reaction proceeds as in an acid solution (this vol., i, 704), $CHAc(C_5H_{11})\cdot CO_2Et + EtNO_2 = Me\cdot CO_2Et + NOH\colon C(C_5H_{11})\cdot CO_2Et$. If amyl nitrite is used instead of ethyl nitrite, mixed esters are obtained by partial substitution of amyl for ethyl.

The results indicate that if the reaction of nitrous acid with the *a*-substituted-*β*-ketonic esters takes place under such conditions that the alkyl group is not hydrolysed at all or is hydrolysed in presence of an acid, the products are an acid and the oxime of a substituted glyoxylic ester, whilst if during the reaction the alkyl group is hydrolysed so as to form a salt, $R\cdot CO\cdot CHR'\cdot CO_2M$, the products are carbon dioxide and the monoxime of an *a*-diketone. C. H. B.

Dimethylene Tartrate. Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 130346).—*Dimethylene tartrate*,

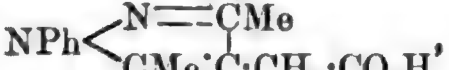


$$CH_2{<}\begin{matrix}O\cdot CO & CO\cdot O\\ O\cdot CH\cdot & CH\cdot O\end{matrix}{>}CH_2,$$

produced by heating tartaric acid with paraformaldehyde or trioxymethylene at 140—150° and treating the clear solution thus obtained with concentrated sulphuric acid at 60°, crystallises from alcohol, acetone, or chloroform in needles, melts at 120°, and boils without decomposition at 296°. It is slowly hydrolysed by water and more readily attacked by solutions of the alkali hydroxides and carbonates. The substance may also be obtained by adding to an aqueous solution of tartaric acid and formaldehyde sufficient sulphuric acid or phosphoric acid to combine with the whole of the water. Hydrochloric acid does not induce this condensation. G. T. M.

Action of Halogen Esters and Ketones on Sodioacetylacetone.

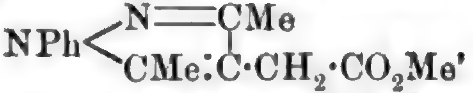
By FR. MARCH (*Ann. Chim. Phys.*, 1902, [vii], 26, 295—366. Compare Abstr., 1900, i, 374; 1901, i, 312, 596, and this vol., i, 484).—1-*Phenyl*-3 : 5-*dimethylpyrazole*-4-*acetic acid*,



$$\mathrm{NPh}{<}\begin{matrix}\mathrm{N{=\!=}CMe}\\ \mathrm{CMe{:}C{\cdot}CH_2{\cdot}CO_2H}\end{matrix},$$

produced by hydrolysing the corresponding ethyl ester with concentrated sodium hydroxide solution, separates from ether in colourless crystals melting at 140—141°; its *copper* salt, $Cu(C_{13}H_{13}O_2N_2)_2$, is a violet compound.

Methyl 1-*phenyl*-3 : 5-*dimethylpyrazole*-4-*acetate*,

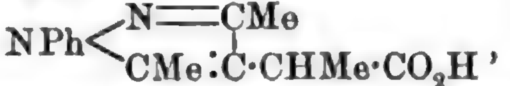


$$\mathrm{NPh}{<}\begin{matrix}\mathrm{N{=\!=}CMe}\\ \mathrm{CMe{:}C{\cdot}CH_2{\cdot}CO_2Me}\end{matrix},$$

resulting from the interaction of methyl ββ-diacetylpropionate, phenylhydrazine hydrochloride, and sodium acetate in dilute methyl alcohol, crystallises from ether in prisms melting at 65°; it is insoluble in water, but readily dissolves in methyl or ethyl alcohol, and yields the preceding acid on hydrolysis.

Ethyl ββ-diacetyl-α-methylpropionate, $CHAc_2{\cdot}CHMe{\cdot}CO_2Et$, prepared by heating at 120—140° ethyl α-bromopropionate and sodioacetylacetone, is an almost colourless oil boiling at 128—130° under 10 mm., and at 149—151° under 33 mm. pressure; it has a sp. gr. 1·067 at 15°, and develops a coloration with ferric chloride; its *copper* derivative, $(C_{10}H_{15}O_4)_2Cu$, is unstable. The ester, when treated with sodium ethoxide, is hydrolysed into sodium acetate and ethyl α-methyllævulate; the action of sodium hydroxide on the ester gives rise to sodium α-methyllævulate.

1-*Phenyl*-3 : 5-*dimethylpyrazole*-4-α-*propionic acid*,

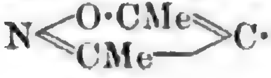


$$\mathrm{NPh}{<}\begin{matrix}\mathrm{N{=\!=}CMe}\\ \mathrm{CMe{:}C{\cdot}CHMe{\cdot}CO_2H}\end{matrix},$$

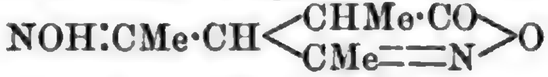
produced by hydrolysing the oily condensation product of the interaction of the preceding ester and phenylhydrazine crystallises from alcohol and melts at 129—130°.

The *disemicarbazone* of ethyl α-methyl-ββ-diacetylpropionate is a white, crystalline compound melting at 207—208°.

The action of hydroxylamine on the ester gives rise to two products, the *dioxime*, $(NOH{:}CMe)_2CH{\cdot}CHMe{\cdot}CO_2Et$, crystallising in needles and melting at 133°, and *ethyl* 3 : 5-*dimethyloxazole*-4-α-*propionate*,



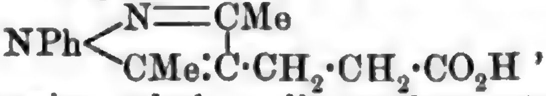
$\mathrm{N}{<}\begin{matrix}\mathrm{O{\cdot}CMe}\\ \mathrm{CMe{-\!-}}\end{matrix}{>}\mathrm{C{\cdot}CHMe{\cdot}CO_2Et}$, a liquid boiling at 143—145° under

21 mm. pressure; the corresponding *acid*, readily obtained by alkali hydrolysis, forms colourless crystals melting at 106°; its *copper* salt, $(C_8H_{10}O_3N_2)_2Cu$, is a light green, insoluble substance melting at 154—155°. When the condensation with hydroxylamine is effected by boiling the ester with excess of this reagent and potassium carbonate, another *compound* is formed which probably has the formula  $NOH\!:\!CMe\cdot CH\left<\begin{array}{l}CHMe\cdot CO\\ CMe{=\!=}N\end{array}\right>O$; this product crystallises in needles and melts at 202—204°.

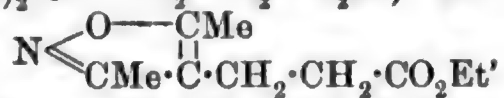
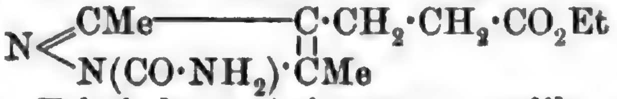
Methyl γγ-diacetylbutyrate, $CHAc_2\cdot CH_2\cdot CH_2\cdot CO_2Me$, a pale yellow liquid boiling at 160—161° under 24 mm. pressure, is produced by condensing methyl β-chloropropionate with sodioacetylacetone; it readily dissolves in dilute sodium carbonate solution and develops a red coloration with ferric chloride; the silky, green, *copper* derivative is insoluble in water, alcohol, or ether, but readily dissolves in chloroform; it melts at 220°.

Ethyl γγ-diacetylbutyrate boils at 154—155° under 15 mm. pressure, develops a coloration with ferric chloride, and yields a silky, green, *copper* derivative dissolving in chloroform and melting at 209°; when treated with alkali hydroxides, this ester gives rise to γ-acetylbutyric acid. By the action of sodium ethoxide and methyl iodide, the ester loses an acetyl group and furnishes *ethyl γ-acetyl-γ-methylbutyrate*, $CHMeAc\cdot CH_2\cdot CH_2\cdot CO_2Et$, a pale yellow liquid boiling at 117—118° under 23 mm. pressure and having a sp. gr. 1·004 at 0°/0°; the corresponding *acid* boils at 168—169° under 22 mm. pressure and has a sp. gr. 1·114 at 0°/0°; its *semicarbazone*, $C_8H_{15}O_3N_3$, melts indefinitely at 152—158°.

1-*Phenyl*-3 : 5-*dimethylpyrazole*-4-β-*propionic acid*,



$$NPh\left<\begin{array}{l}N{=\!=}CMe\\ CMe\!:\!C\cdot CH_2\cdot CH_2\cdot CO_2H\end{array}\right.,$$

produced by condensing ethyl γγ-diacetylbutyrate with phenylhydrazine and hydrolysing the oily product with potassium hydroxide, crystallises from dilute alcohol, &c., in colourless needles and melts at 134—135°. The *dioxime*, $(NOH\!:\!CMe)_2\cdot CH\cdot CH_2\cdot CH_2\cdot CO_2Et$, and *ethyl* 3 : 5-*dimethyloxazole*-4-β-*propionate*,  $N\left<\begin{array}{l}O{-\!-}CMe\\ CMe\cdot C\cdot CH_2\cdot CH_2\cdot CO_2Et\end{array}\right.$, are produced by the action of hydroxylamine on ethyl diacetylbutyrate; the former crystallises in colourless prisms melting at 108—110°, the latter is an oil boiling at 157—158° under 23 mm. pressure and yielding on hydrolysis the corresponding acid melting at 109—110°. The ester, when condensed with semicarbazide, gives rise to the *compound*  $N\left<\begin{array}{l}CMe{-\!-\!-\!-}C\cdot CH_2\cdot CH_2\cdot CO_2Et\\ N(CO\cdot NH_2)\cdot CMe\end{array}\right.$, which melts at 114—115°. Ethyl bromo*iso*butyrate, unlike its lower homologues, does not react with sodioacetylacetone.

Acetonylacetylacetone, $CHAc_2\cdot CH_2\cdot Ac$, produced by condensing chloroacetone and sodioacetylacetone, boils at 156° under 35 mm. pressure; its *copper* derivative crystallises from chloroform in needles melting at 267—268° and is somewhat volatile. G. T. M.

Coloured Organic Ferric Compounds. By ARTHUR HANTZSCH and CECIL H. DESCH (*Annalen*, 1902, **323**, 1—31).—Determinations of the electrical conductivity of aqueous solutions of ferric acetylacetone indicate that the substance is practically a non-electrolyte, the values obtained being $\epsilon_{256} = 0{\cdot}72$, and $\epsilon_{1024} = 1{\cdot}68$. The compound is very slowly decomposed by hydrochloric acid, even when this reagent is in excess, and the change has been studied quantitatively by determining the electrical conductivities of solutions of the substance with one, two, or three molecular proportions of the acid.

The decomposition of the salt by hydrogen chloride in anhydrous solvents is instantaneous and complete, but when the reagent is gradually added the change is seen to occur in three stages, the light red solution becoming deep red, then reddish-violet, and finally assuming the pale yellow colour of ferric chloride. The colour changes correspond with the gradual transformation of $Fe(C_5H_7O_2)_3$ into $Fe(C_5H_7O_2)_2Cl$ and $Fe(C_5H_7O_2)Cl_2$.

Aluminium acetylacetone is as poor a conductor of electricity as its ferric analogue, and is even less readily attacked by hydrochloric acid. *Ethyl ferribenzoylacetate*, $Fe(C_{11}H_{11}O_3)_3$, obtained as an oily residue by extracting with ether a concentrated solution of ferric chloride, sodium acetate, and ethyl benzoylacetate in dilute alcohol, slowly becomes solid and separates from its alcoholic solution in deep red crystals melting at 128°. *Ethyl ferrioxaloacetate*, $Fe(C_8H_{11}O_5)_3$, prepared in a similar manner, separates as a lustrous, dark red, hygroscopic powder on diluting its alcoholic solution with water.

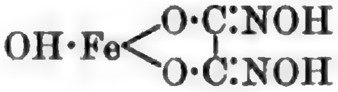
Although ferric chloride and ethyl acetoacetate develop an intense coloration, the amount of ethyl ferriacetoacetate actually produced in aqueous solutions is but very small; the reaction takes place, however, to a greater extent when the reagents are dissolved in alcohol.

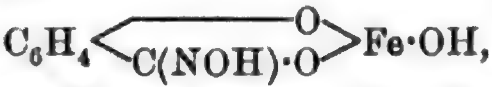
Ferrisalicylic acid, $OH{\cdot}Fe(O{\cdot}C_6H_4{\cdot}CO_2H)_2$, produced by shaking an ethereal solution of salicylic acid with a concentrated aqueous solution of ferric chloride and sodium acetate, crystallises from the ethereal extract in red prisms which contain 1 mol. of ether. The compound, when freed from ether, has a purple colour and dissolves in water to a reddish-violet solution; it behaves as an acid salt, dissolving in solutions of the alkali hydroxides without decomposition.

o-Methoxybenzoic acid does not react with ferric chloride; methyl salicylate and salicylaldehyde develop colorations with ferric chloride, but the products could not be isolated. Electrolytic determinations show that the amount of coloured salt formed from phenol and ferric chloride is very small; this is also true of resorcinol, but its isomerides show more tendency to enter into reaction, the amount of double decomposition being greatest in the case of catechol.

Pyrogallol and *p*-aminophenol, when treated with ferric acetate, yield violet-black substances which are insoluble in water or the organic solvents, but dissolve in hydrochloric acid to a yellow solution. Ethyl dicarboxyglutaconate and excess of ferric chloride in dilute alcoholic solution develop a blue coloration, but the actual amount of double decomposition is very small.

Ferric acetylhydroxamate, $Fe(C_2H_4O_2N)_3$, separates in deep red prisms from an alcoholic solution of acetylhydroxamic acid and ferric ethoxide; it readily dissolves in water to a bluish-red solution; its equivalent conductivities at 25° are $\epsilon_{100\cdot8}=7{\cdot}5$, and $\epsilon_{201\cdot6}=8{\cdot}4$ respectively. The salt is accordingly a "half-electrolyte"; its degree of ionisation, although far less than that of a normal salt, is greatly in excess of that of ferric acetylacetone. The aqueous solution of the salt gives no precipitate with potassium ferrocyanide, but ferric hydroxide is slowly deposited on adding strong ammonia solution; hydrochloric acid develops an intense violet coloration, which disappears on adding excess of the reagent.

Ferric oxalodihydroxamate,  $\mathrm{OH{\cdot}Fe}\left\langle\begin{array}{l}\mathrm{O{\cdot}C{:}NOH}\\ \mathrm{O{\cdot}C{:}NOH}\end{array}\right.$, produced by the interaction of oxalodihydroxamic acid and ferric acetate, separates as a deep violet precipitate, dissolving in excess of ferric chloride solution to a violet solution. The ferric salt is insoluble in water, alcohol, or ether, explodes on heating, and dissolves in solutions of the alkali hydroxides without decomposition.

Ferric salicylhydroxamate,  $\mathrm{C_6H_4}\left\langle\begin{array}{r}\mathrm{O}\\ \mathrm{C(NOH){\cdot}O}\end{array}\right\rangle\mathrm{Fe{\cdot}OH}$, resembles the preceding salt and dissolves without decomposition in solutions of the alkali hydroxides.

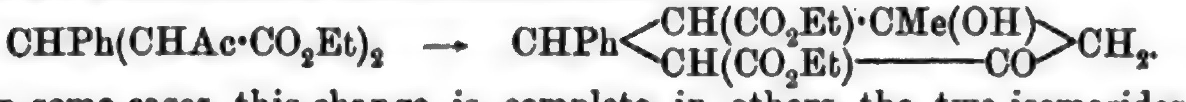
Lanthanum acetylacetone, $\mathrm{La(C_5H_7O_2)_3}$, is prepared by dissolving freshly precipitated lanthanum oxide in a dilute alcoholic solution of acetylacetone; the reaction is accompanied by development of heat, and the salt crystallises, on cooling, in white needles. In solution, the sparingly soluble lanthanum salt is more highly ionised than its ferric and aluminium analogues; it is more rapidly attacked by hydrochloric acid than these substances.

Acetylacetone and catechol show a slight tendency to interact with boric acid.

Solutions of colloidal ferric hydroxychloride, which have a marked acid reaction and a noteworthy electrical conductivity, contain their chlorine in a non-ionised condition, so that it is not precipitated as silver chloride until after acidifying. It must therefore be supposed that this chlorine exists in these solutions in the form of a complex chloroferric acid. Chlorine exists in a similar condition in the coagula obtained by carefully adding ammonia to aqueous solutions of aluminium chloride until the turbidity produced remains undissolved.

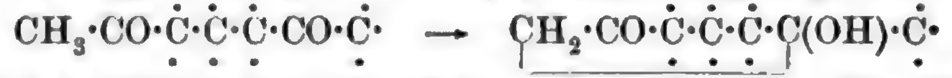
G. T. M.

δ-(1:5-)-Diketones. By Paul Rabe and Fritz Elze (*Annalen*, 1902, **323**, 83—112).—The δ- or 1:5-diketones containing a methyl group attached to one of their carbonyl radicles readily undergo rearrangement into *cyclo*hexanolones. For example, diethyl benzylidenebisacetoacetate, a condensation product from benzaldehyde and ethyl acetoacetate, gives the reactions of diethyl 3-methyl-5-phenyl-*cyclo*hexan-3-ol-1-one-4:6-dicarboxylate, the transformation being due to an intramolecular aldol condensation,

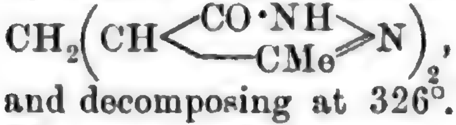


$$\mathrm{CHPh(CHAc{\cdot}CO_2Et)_2}\ \longrightarrow\ \mathrm{CHPh}\left\langle\begin{array}{l}\mathrm{CH(CO_2Et){\cdot}CMe(OH)}\\ \mathrm{CH(CO_2Et)\text{———}CO}\end{array}\right\rangle\mathrm{CH_2}.$$

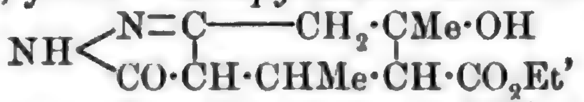
In some cases, this change is complete, in others, the two isomerides exist together in a condition of equilibrium. Evidence of the inverse transformation is furnished by Knoevenagel's researches (Abstr., 1899, i, 214). The formation of the cyclic isomeride is brought about by the action of piperidine, sodium ethoxide, or other compounds of a similar nature. The δ-diketones, which have undergone complete rearrangement, are tabulated and their appropriate designations as cyclic compounds are indicated. The nature of the change involved in this rearrangement is indicated by the following diagram.



$$CH_3\cdot CO\cdot\dot{\underset{\cdot}{C}}\cdot\dot{\underset{\cdot}{C}}\cdot\dot{\underset{\cdot}{C}}\cdot CO\cdot\dot{\underset{\cdot}{C}}\cdot \longrightarrow CH_2\cdot CO\cdot\dot{\underset{\cdot}{C}}\cdot\dot{\underset{\cdot}{C}}\cdot\dot{\underset{\cdot}{C}}\cdot C(OH)\cdot\dot{\underset{\cdot}{C}}\cdot$$

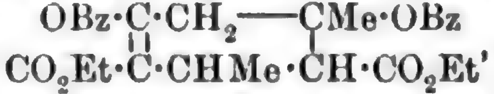
Diethyl methylenebisacetoacetate, when treated with hydrazine hydrate in alcoholic solution, yields 4-*methylenebis-3-methyl-5-pyrazolone*,  $CH_2\left(CH<\begin{matrix}CO\cdot NH\\ CMe\end{matrix}>N\right)_2$, a substance separating in rhombic crystals and decomposing at 326°. When left in contact with pyridine, the diketone slowly becomes transformed into diethyl 3-methyl*cyclo*hexan-3-ol-1-one-4 : 6-dicarboxylate, and the rate at which this change proceeds is indicated by treating separate portions of the product at successive intervals of time with hydrazine hydrate. The yield of bispyrazolone steadily diminishes.

Diethyl ethylidenebisacetoacetate is obtained as a viscid oil by mixing together ethyl acetoacetate, acetaldehyde, and a small amount of piperidine at −15° to +5°; the aliphatic nature of the product is demonstrated by the formation of 4-ethylidenebis-3-methyl-5-pyrazolone, which crystallises in prismatic needles and decomposes at 250° (compare Rosengarten, Abstr., 1894, i, 547). The transformation product, *diethyl* 3 : 5-*dimethyl*cyclo*hexan*-3-*ol*-1-*one*-4 : 6-*dicarboxylate*, melting at 79—80°, and described by Knoevenagel as the unaltered diethyl ethylidenebisacetoacetate (Abstr., 1895, i, 50), when treated with hydrazine hydrate, yields a *monopyrazolone* derivative,



$$NH<\begin{matrix}N{=}C\text{———}CH_2\cdot CMe\cdot OH\\ CO\cdot CH\cdot CHMe\cdot CH\cdot CO_2Et\end{matrix},$$

which crystallises in needles, decomposes at 256°, and dissolves either in acid or alkaline solutions.

The cyclic ketone reacts in its enolic form when treated in ethereal solution with sodium, benzoyl chloride, and pyridine, giving rise to the *dibenzoyl* derivative,  $\begin{matrix}OBz\cdot C\cdot CH_2\text{———}CMe\cdot OBz\\ CO_2Et\cdot C\cdot CHMe\cdot CH\cdot CO_2Et\end{matrix}$, a pale yellow oil boiling at 175—185° under the atmospheric pressure and partly solidifying at the ordinary temperature. The *phenylcarbamide*,

$$C_{14}H_{21}O_5\cdot O\cdot CO\cdot NHPh,$$

of the cyclic ketone, produced by allowing its generators to interact for 5 months at the ordinary temperature, is a crystalline substance melting at 210°.

The three isomeric β_1-, β_2-, and β_3-esters, obtained by condensing ethyl acetoacetate with benzaldehyde in the presence of pyridine, are now regarded as stereoisomeric diethyl 3-methyl-5-phenyl*cyclo*hexan-3-ol-1-one-4 : 6-dicarboxylates. The *phenylhydrazone* of the β_1-modification crystallises from alcohol in needles decomposing at 168—171°. The β_1- and β_2-esters both yield the same *pyrazolone*, $C_{17}H_{20}O_4N_2$, melting at 257°, which is identical with that obtained from the isomeric α_1-ester (compare Rabe, Abstr., 1901, i, 34). The β_3-ester gives rise to an isomeric *pyrazolone* crystallising in white needles and melting at 140°.

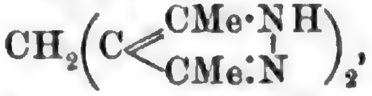
Diethyl 3-methyl-5-*m*-nitrophenyl*cyclo*hexan-3-ol-1-one-4 : 6-dicarboxylate, described by Knoevenagel and Schürenberg as diethyl *m*-nitrobenzylidenebisacetoacetate (Abstr., 1899, i, 214), when heated with an alcoholic solution of hydrazine hydrate, yields a *pyrazolone*, $C_{17}H_{19}O_6N_3$, crystallising in prisms melting at 260°; this forms an insoluble sulphate and a sodium derivative.

p-Nitrobenzaldehyde and ethyl acetoacetate give rise to two stereoisomeric *cyclo*hexanone derivatives; the β_1-ester, first isolated by Knoevenagel (*loc. cit.*), melts at 164° and yields a *pyrazolone* separating from alcohol in rhombic crystals and melting at 280°; the β_2-ester, melting at 152°, furnishes a *pyrazolone* crystallising in lustrous leaflets decomposing at 260°.

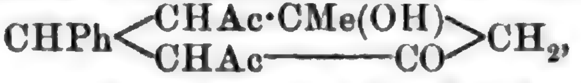
The ethereal alkylidenebisbenzoylacetates, unlike the corresponding condensation products from ethyl acetoacetate, are not affected by piperidine. Diethyl methylenebisbenzoylacetate (m. p. 86°), when treated with hydrazine hydrate, furnishes a theoretical yield of 4-*methylenebis*-3-*phenyl*-5-*pyrazolone*, which crystallises from alcohol in leaflets, decomposes at 280°, and dissolves in dilute acid or solutions of the alkali hydroxides.

4-*Benzylidenebis*-3-*phenyl*-5-*pyrazolone*, $C_{25}H_{20}O_2N_4$, is a very soluble pyrazolone obtained by condensing diethyl benzylidenebisbenzoylacetate with hydrazine hydrate; 4-*benzylidenebis*-1-p-*bromophenyl*-3-*phenyl*-5-*pyrazolone*, $C_{37}H_{28}O_2N_4Br_2$, is produced from the same δ-diketone by the action of *p*-bromophenylhydrazine; it melts and decomposes at 290°.

The authors have obtained methylenebisacetylacetone only in the form of a viscid oil from which, after some months, a small quantity of a crystalline substance separates melting at 181° (compare Scholtz, Abstr., 1898, i, 43, and Knoevenagel, *ibid.*, i, 449).

4-*Methylenebis*-3 : 5-*dimethylpyrazole*,  $CH_2\left(C<\begin{array}{l}CMe\cdot NH\\ CMe{:}N\end{array}\right)_2$, prepared by the action of hydrazine hydrate on the preceding δ-diketone, crystallises in rhombohedra and melts at 280°; it readily dissolves in alcohol, but is only sparingly soluble in water. The δ-diketone undergoes transformation under the influence of piperidine, but neither the *cyclo*hexanone nor its pyrazole could be obtained in a state of purity.

4 : 6-*Diacetyl*-5-*phenyl*-3-*methyl*cyclo*hexan*-3-*ol*-1-*one*,



$$CHPh<\begin{array}{l}CHAc\cdot CMe(OH)\\ CHAc\text{———}CO\end{array}>CH_2,$$

obtained by Knoevenagel, and also by Schiff (Abstr., 1895, i, 50, and 1900, i, 39), by condensing acetylacetone with benzaldehyde, is shown to be a cyclic compound by yielding a *pyrazole*, $C_{17}H_{28}O_2N_2$, with hydrazine hydrate; this compound crystallised in prisms and decomposed at 220°; the product of this reaction is at first contaminated with an azine, which is destroyed by boiling with dilute hydrochloric acid.

G. T. M.

[a-Glucoheptose.] By JULIUS WOHLGEMUTH (*Zeit. physiol. Chem.*, 1902, **35**, 568—579).—The following compounds of a-glucoheptose are described: the *phenylmethylhydrazone* forms white crystals melting at 150° and the *diphenylhydrazone* white crystals melting at 140°; the osazone in pyridine alcohol mixture has the rotation +0°30′. a-Glucoheptose does not give the resorcinol reaction, but with orcinol and phloroglucinol its reactions are very like those of the pentoses; these two reactions are believed to be characteristic of sugars with an uneven number of carbon atoms. W. D. H.

The Influence of Pressure on the Inversion of Cane Sugar by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, **54**, 352—353).—Increase of pressure up to 400—800 atmospheres very slightly accelerates the inversion of cane sugar by sucrase. According to Röntgen, increase of pressure has the opposite effect on inversion by acids. W. D. H.

Influence of the Concentration of Cane Sugar on the Rapidity of Inversion by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, **54**, 610—611).—No proportionality was observed between the concentration of solution of cane sugar and the rapidity of its inversion by sucrase, as described by Brown (Trans., 1902, **81**, 373). W. D. H.

Action of Sodium Chloride on Inversion by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, **54**, 611—612).—Sodium chloride is taken as an example of a neutral salt; a constant quantity of salt inhibits inversion to a greater extent when a strong solution of cane sugar is employed than when a weak one is used. Its inhibiting action is greater when the amount of sucrase present is small.
W. D. H.

Action of Neutral Salts on the Inversion of Cane Sugar by Sucrase. By VICTOR HENRI (*Compt. rend. Soc. Biol.*, 1902, **54**, 353—354).—The results show that various neutral salts exercise an inhibiting power on the rate of inversion of cane sugar by sucrase, and that there is a parallelism between this action and their capacity of precipitating colloids. W. D. H.

Velocity of Hydrolysis of Acetylated Monoses and Bioses. By ROBERT KREMANN (*Monatsh.*, 1902, **23**, 479—488. Compare this vol., i, 134).—The rate of hydrolysis, k, is determined for the penta-acetyldextrose and -galactose, tetra-acetylgalactose, tetra-acetylchlorodextrose, and -chlorogalactose, and octo acetyl-lactose, -maltose, and -sucrose with sodium hydroxide in 96 per cent. alcohol. The value of k for tetra-acetylgalactose remains almost constant throughout the hydrolysis, but for the other acetyl compounds k diminishes gradually, in some cases to half of its original value. This is due to a difference in the rate of hydrolysis of the different acetyl groups, the most reactive acetyl group of penta-acetylgalactose being absent in the tetra-acetyl derivative. As the value of k is smaller for the acetyldextroses than for the acetylgalactoses, the acetyl groups in the former are less reactive, this observation is made use of to explain the formation of tetra-acetylnitrodextrose, and the non-formation of tetra-acetylnitrogalactose, from the corresponding chloro-compounds. The value of *k* for octo-acetyl-lactose, which contains a dextrose and a galactose grouping, is greater than that for octo-acetylmaltose, which contains two dextrose groupings. The rate of hydrolysis of octo-acetylsucrose lies between that of octo-acetyl-lactose and that of octo-acetylmaltose, approximating more nearly to the former. Tetra-acetylchlorogalactose is obtained in large, rhombic crystals. Attempts to prepare tetra-acetyldextrose by the action of silver carbonate and metallic sodium on tetra-acetylchlorodextrose resulted apparently in the complete decomposition of the acetyl derivative. G. Y.

Preparation and Properties of Crystallised Gentiobiose. By Émile Bourquelot and Henri Hérissey (*Compt. rend.*, 1902, **135**, 290—292. Compare Abstr., 1901, i, 258).—Gentiobiose has now been obtained in a crystalline form by extracting the crude mixture of sugars produced by the partial hydrolysis of gentianose first with ethyl alcohol to remove lævulose and then with methyl alcohol to dissolve out the new hexobiose. The product crystallising from the latter solvent is white, hygroscopic, and has a bitter taste; it consists of gentiobiose combined with 2 mols. of methyl alcohol and has the formula $C_{12}H_{22}O_{11},2MeOH$. These crystals melt at 85·5—86° (corr.), become solid on further heating, and fuse again at 189—195° to a yellow liquid; the alcohol of crystallisation is removed only by heating at 100—115°. When in solution, the substance exhibits the phenomenon of multirotation, the optical activity of the dextrorotatory solution diminishing to a minimum after 19 hours, the specific rotation at this stage being +8·33°.

Gentiobiose separates from ethyl alcohol in crystals having the composition $C_{12}H_{22}O_{11}$. In this form it also exhibits multirotation, but the optical activity of its solution increases until a maximum is reached after 6 hours, giving $[\alpha]_D$ 9·61°.

This value of the specific rotation corresponds with that obtained for the crystals separating from methyl alcohol, providing that allowance is made for the solvent contained in this preparation.

G. T. M.

Action of Enzymes on Hemicelluloses. By J. Grüss (*Chem. Centr.*, 1902, i, 1277; from *Woch. Brauerei*, **19**, 243—245).—Galactose is formed by the action of diastase powder prepared by Lintner's method on tragacanth, and under similar conditions mannan, the hemicellulose obtained from the endosperm of date seeds, yields mannose. By the action of the enzyme contained in the date itself, mannan is converted into mannose about twice as quickly as by a 5 per cent. solution of Lintner's diastase. Hence the hemicelluloses contained in barley are attacked by diastase, and by its prolonged action the same sugars are formed as those obtained by the action of acids.

The original paper also contains a description of experiments in which similar results were obtained by using two diastases prepared from barley malt and oat malt by Heinzelmann's methods.

E. W. W.

Organic Vapour in the Air. By H. HENRIET (*Compt. rend.*, 1902, **135**, 101—103).—Air contains an organic vapour which seems to be a substituted formamide, NHR·CHO. It is slowly converted into carbon dioxide by the action of the oxygen of the air, and if the air is moist and the moisture is condensed, the resulting water reduces silver nitrate solution on boiling, converts mercuric chloride into mercurous chloride, and reduces gold chloride and alkaline potassium permanganate. With Nessler's reagent, it gives a yellowish-green opalescence, especially if the liquid is previously heated with a small quantity of potassium hydroxide or of hydrochloric acid. The reducing power disappears if the condensed moisture is evaporated with sulphuric acid; if it is evaporated with hydrochloric acid, the residue gives the *iso*nitrile reaction for primary amines. C. H. B.

Dialkylamides of *iso*Valeric and α-Bromo*iso*valeric Acids. ARTHUR LIEBRECHT (D.R.-P. 129967).—iso*Valerodimethylamide*, prepared by the action of *iso*valeryl chloride on dimethylamine dissolved in ether, boils at 188—192° under the ordinary pressure; the corresponding *diethylamide* and the *di*iso*amylamide* boil at 210—212° and 270—275° respectively under the ordinary pressure; the latter derivative is produced by heating di*iso*amylamine with *iso*valeric anhydride, *iso*valeroamide, or ethyl *iso*valerate under pressure.

*α-Bromo*iso*valerodiethylamide* results from the interaction of diethylamine and α-bromo*iso*valeryl bromide in ethereal solution; it boils at 130—135° under 20 mm. pressure. G. T. M.

Hydroxy*iso*propylphosphinic Acid. By CH. MARIE (*Compt. rend.*, 1902, **135**, 106—108).—The methyl ester of hydroxy*iso*propylphosphinic acid (this vol., i, 431) melting at 76° and the ethyl ester which is liquid at the ordinary temperature are readily prepared by the action of the corresponding iodides on the silver salt. They decompose when distilled, yielding acetone and products which are still under investigation. When the esters are treated with an alkali hydroxide, decomposition takes place in two well marked stages, the first change being practically instantaneous, whilst the other necessitates the addition of a large excess of alkali and the prolonged boiling of the liquid. When treated with benzoyl chloride in presence of excess of pyridine, the acid yields *benzoyl*iso*propylphosphinic acid*, $OBz{\cdot}C_3H_6{\cdot}PO_3H_2$, a crystallisable compound which melts at 102° and forms a white, crystallisable silver salt, $OBz{\cdot}C_3H_6{\cdot}PO_3Ag_2$. The above facts show that the constitution of the acid is $OH{\cdot}CMe_2{\cdot}PO(OH)_2$.

C. H. B.

Separation of Cyclic Aromatic Oxides or Sulphides from Coal Tar Hydrocarbons. AKTIEN-GESELLSCHAFT FÜR THEER- & ERDÖL-INDUSTRIE (D.R.-P. 130679).—Mixtures of hydrocarbons containing cyclic oxides or sulphides are fused with potassium hydroxide, the fused product being subsequently lixiviated with water. Under these conditions, the oxides become converted into the soluble potassium derivatives of the diphenols, $O(C_6H_4)_2 + 2KOH = C_{12}H_8(OK)_2 + H_2O$, and are thus separated from the insoluble hydrocarbons. G. T. M.

Derivatives of 1 : 3-Dichloro-4 : 6-dinitrobenzene. By JAN JOHANNES BLANKSMA and P. C. E. MEERUM TERWOGT (*Rec. trav. chim.*, 1902, **21**, 286—291).—The authors have studied the nitration products of *m*-dichlorobenzene. By the action of sodium ethoxide on 1 : 3-dichloro-4 : 6-dinitrobenzene, 1 : 3-diethoxy-4 : 6-dinitrobenzene (diethyl-4 : 6-dinitroresorcinol) is obtained melting at 133°. 1 : 3-Dimethoxy-4 : 6-dinitrobenzene is formed in a similar manner; it melts at 157°, even after repeated crystallisation from methyl alcohol, the melting point given by Loring Jackson and Warren (Abstr., 1891, 1024) being 167°. On heating this compound with alcoholic ammonia, the corresponding 4 : 6-dinitro-*m*-phenylenediamine is obtained, and on heating it with hydrochloric acid in a sealed tube, 4 : 6-dinitroresorcinol is formed. When 1 : 3-dichloro-4 : 6-dinitrobenzene is heated with methylamine in alcoholic solution, the chlorine atoms are replaced and there is produced 4 : 6-*dinitro*-1 : 3-*dimethyl*-m-*phenylenediamine*, which forms small, yellow crystals, sparingly soluble in alcohol or acetic acid, and does not melt even at 280°. On dissolving the latter in nitric acid and heating the solution for a short time, 2 : 4 : 6-trinitro-*m*-phenylene-1 : 3-dimethyldinitroamine, $C_6H(NMe{\cdot}NO_2)_2(NO_3)_3$, is formed.

A. F.

Preparation of Aromatic Sulphinic Acids. BASLER CHEMISCHE FABRIK (D.R.-P. 130119).—The aromatic sulphinic acid is obtained by adding to the cold diazo-solution a 40 per cent. solution of sodium hydrogen sulphite and excess of alcoholic sulphurous acid containing a small quantity of cupric sulphate or other compound of copper. The reaction occurs at 0—20° in the case of aniline, *o*-toluidine, or methyl anthranilate, but more stable diazo-salts require a higher temperature. The solution obtained from *o*-anisidine must be warmed to 30°.

G. T. M.

Nitrodihydrophenanthrene. JULIUS SCHMIDT (D.R.-P. 129990. Compare Abstr., 1901, i, 76).—Finely divided phenanthrene, when mixed with the liquefied crude product of the action of nitric acid on starch or arsenious oxide, takes up the elements of nitrous acid and yields *nitrodihydrophenanthrene*, $C_{14}H_{11}O_2N$; this substance is a yellow, crystalline powder, softening at 70° and decomposing at 100°; it readily dissolves in the ordinary organic solvents. G. T. M.

Reduction of Aromatic Nitro-compounds to Amines. C. F. BOEHRINGER & SÖHNE (D.R.-P. 130742).—Nitrobenzene, when gradually added to copper powder suspended in concentrated sodium chloride solution contained in the cathode compartment of an electrolytic cell, is quantitatively reduced to aniline at 80—100° by a current of 1500 amperes per square metre and 5 volts. A copper cathode is employed, whilst the anode compartment contains a carbon anode surrounded by concentrated sodium chloride solution.

Under similar conditions, *o*-nitrotoluene and *a*-nitronaphthalene readily yield *o*-toluidine and *a*-naphthylamine, whilst *m*-nitroaniline is reduced to *m*-phenylenediamine, the yield being 80 per cent.

G. T. M.

Action of Formaldehyde [on Ethylaniline]. By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1902, **26**, 606. Compare Abstr., 1900, i, 436).—A mixture of monoethylaniline, formaldehyde, and hydrochloric acid forms, after some days, the compound $NEtPh{\cdot}CH_2Cl$. This melts at 250° and is soluble in hot water; alkali hydroxides added to its dilute aqueous solution separate a base which is soluble in chloroform and may be obtained pure by precipitating the solution with ether.

Similar compounds may be obtained in this manner from the esters of the three aminobenzoic acids, and mention is made of the production of compounds by the action of formaldehyde on benzoylthymol, phenylhydrazine, and acetylphenylhydrazine.

By treating resacetophenone for 2 hours with formaldehyde and hydrochloric acid and boiling the product with xylene, an insoluble compound is obtained which, however, dissolves in chloroform and is precipitated from the solution by addition of ether. The xylene contains a second product which separates as a white, crystalline substance melting at 245—250° and is soluble in the alkali hydroxides.

L. DE K.

Iodo-derivatives of Aromatic Aminosulphonic Acids. KALLE & Co. (D.R.-P. 129808).—The aromatic amines, when treated with iodine monochloride, give rise to tarry products; their monosulphonic acids, on the other hand, furnish well-defined iodo-derivatives when treated with hydrochloric acid solutions of this reagent.

Iodosulphanilic acid crystallises from its concentrated aqueous solutions in small, white needles. *Di-iodosulphanilic acid*, resulting from the action of excess of iodine monochloride on sulphanilic acid, separates from dilute aqueous solutions on the addition of sodium chloride. *Di-iodometanilic acid* crystallises from water in colourless leaflets. The diazo-compounds of these iodoaminosulphonic acids are yellow.

G. T. M.

Trisubstituted Naphthalene Derivatives. By ARTURO JACCHIA (*Annalen*, 1902, **323**, 113—134).—6-Nitro-*β*-naphthylamine-8-sulphonic acid is most conveniently obtained by nitrating *β*-naphthylamine-8-sulphonic acid dissolved in concentrated sulphuric acid with potassium nitrate. The 2 : 6-diaminonaphthalene-8-sulphonic acid produced by reducing the nitro-compound yields 2 : 6-diaminonaphthalene on treatment with sodium amalgam and was formerly supposed to be identical with the compound prepared by heating 2 : 6-dihydroxynaphthalenesulphonic acid with ammonia under pressure (D.R.-P. 72222). An examination of the latter diamino-acid showed that the commercial product consists of a mixture of free sulphonic acids and their sodium salts, the principal constituent of which is a diaminonaphthalenedisulphonic acid. This substance, which is insoluble in alcohol, crystallises from water in leaflets having a silvery lustre and the composition $C_{10}H_4(NH_2)_2(SO_3H)_2,4\frac{1}{2}H_2O$; when the aqueous solution is treated with sodium amalgam, 2 : 6-diaminonaphthalene is produced.

The *ammonium* salt of 6-nitro-β-naphthylamine-8-sulphonic acid crystallises in dark red, anhydrous prisms; the *barium* salt separates in red crystals with $4\frac{1}{2}H_2O$.

The *anhydride* of 6-*nitro*-2-*diazonaphthalene*-8-*sulphonic acid*, obtained by diazotising the preceding ammonium salt, is very sparingly soluble in cold water; it combines with aniline, yielding a red colouring matter, and when boiled with water gives rise to 6-*nitro-β-naphthol*-8-*sulphonic acid*, $NO_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H,4H_2O$, which crystallises from water in light yellow prisms and retains $2H_2O$ even at 150°; the *potassium* salt, $NO_2{\cdot}C_{10}H_5(OH){\cdot}SO_3K$, separates in anhydrous, orange prisms; the *barium* salt, $[NO_2{\cdot}C_{10}H_5(OH){\cdot}SO_3]_2Ba,6\frac{1}{2}H_2O$, crystallises in dark yellow prisms; the *sodium* salt is less definite and crystallises either with 5 or $6H_2O$.

6-*Amino-β-naphthol*-8-*sulphonic acid*, $NH_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H,H_2O$, produced by reducing the nitro-compound with stannous chloride, crystallises from water in lustrous, grey needles; it is somewhat unstable, and when boiled with an emulsion of barium carbonate yields the barium salt of a dark blue colouring matter, the composition of which approximates to that required by the formula $(C_{40}H_{24}O_{16}N_4S_4)Ba_2$ or $(C_{40}H_{28}O_{16}N_4S_4)Ba_2$.

6-*Amino-β-naphthol* results from the action of sodium amalgam on the preceding sulphonic acid dissolved in an aqueous solution of sulphur dioxide; it crystallises from water in grey flakes which decompose at 190—195° and rapidly assume a blue colour on exposure to the air.

2-*Chloro*-6-*nitronaphthalene*-8-*sulphonic acid*,

$$NO_2{\cdot}C_{10}H_5Cl{\cdot}SO_3H,6H_2O,$$

obtained from 6-nitro-2-diazonaphthalene-8-sulphonic acid by the Sandmeyer reaction, crystallises from water in bright yellow, silky prisms; the *barium* salt crystallises in deep yellow needles with $7H_2O$; the *silver* salt separates in anhydrous, yellowish-brown needles.

6-*Chloro-β-naphthylamine*-8-*sulphonic acid*, $NH_2{\cdot}C_{10}H_5Cl{\cdot}SO_3H$, produced by reducing the preceding nitro compound, is precipitated from the aqueous solution of its sodium salt by excess of hydrochloric acid and crystallises in brown, silky prisms with a violet reflex; the *barium* salt forms very soluble, light brown leaflets. G. T. M.

m-Chloro- and m-Bromo-trinitrophenols. By S. TIJMSTRA (*Rec. trav. chim.*, 1902, 21, 292—293).—On nitrating *m*-chlorophenol with a mixture of nitric and sulphuric acids, 3-chloro-2 : 4 : 6-trinitrophenol is obtained in yellow crystals melting at 119°. In the same manner, *m*-bromophenol gives 3-bromo-2 : 4 : 6-trinitrophenol, which melts at 144°. On treating these compounds with sodium methoxide, the halogen is replaced by the methoxy-group. A. F.

Ionic Phenomena Exhibited by Triphenylmethane Colouring Matters. By OTTO FISCHER (*Chem. Centr.*, 1902, ii, 91; from *Zeit. Farben-Textil-Chem.*, 1902, i, 281).—If an excess of concentrated hydrochloric acid is added to a solution containing a trace of rosaniline, methyl-violet, or malachite-green dissolved in dilute hydrochloric acid, until the liquid becomes yellow, a point may be reached at which the solution no longer shows the slightest coloration when poured into water, but, on the other hand, when added to alcohol, the red, violet, or green ions of the respective dyes are at once apparent. The same phenomena are shown by solutions of the colouring matters in concentrated sulphuric acid (compare also Kehrmann and Wentzel, this vol., i, 89). E. W. W.

7-Amino-β-naphtholsulphonic Acid. LEOPOLD CASSELLA & CO. (D.R.-P. 131526).—7-Amino-β-naphthol readily yields a disulphonic acid, even on treatment with 90 per cent. sulphuric acid; this product readily parts with one of the sulphonic groups on hydrolysis with dilute acids and yields 7-*amino-β-naphtholsulphonic acid*. The *sodium* salt, $OH\cdot C_{10}H_5(NH_2)\cdot SO_3Na,H_2O$, separates in sparingly soluble nodular aggregates; the *diazo*-compound is yellow and sparingly soluble in water. G. T. M.

Preparation of Anthranilic Acid from 4-Sulphoanthranilic Acid. KALLE & CO. (D.R.-P. 129165).—When treated in aqueous solution with sodium amalgam, 4-sulphoanthranilic acid, obtained by the action of sodium hydroxide solution on *o*-nitrotoluene-4-sulphonic acid, readily loses its sulphonic group and gives rise to anthranilic acid. G. T. M.

Preparation of Anthranilic Acid. BASLER CHEMISCHE FABRIK (D.R.-P. 130301, 130302).—Phthalylhydroxylamine (this vol., i, p. 720) or its alkali derivatives, when heated with sodium or potassium carbonate in aqueous or alcoholic solution, becomes converted into the corresponding alkali anthranilate. G. T. M.

ω-Cyanomethylanthranilic Esters. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 129562).—ω-Cyanomethylanthranilic acid,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CN,$$

readily yields its *ethyl* ester when treated at 100° with ethyl bromide in the presence of sodium hydroxide solution or milk of lime; this derivative melts at 89°, whilst the *methyl* ester, prepared by means of methyl sulphate or the methyl ester of an aromatic sulphonic acid, melts at 108°. The methylation with methyl sulphate takes place at 50°. G. T. M.

Action of Sulphites on Aromatic *o*-Hydroxycarboxylic Acids. By HANS BUCHERER (*Zeit. Farben- Textil-Chem.*, 1902, **1**, 477—480. Compare Abstr., 1901, i, 695, and this vol., i, 91).—Although 2-hydroxy-3-naphthoic acid is converted into 2-amino-3-naphthoic acid by the action of ammonia solution at 260° (Möhlau, Abstr., 1894, i, 138), yet, when heated with a mixture of this reagent and ammonium sulphite at 125°, it loses its carboxyl group and becomes converted into β-naphthylamine. The acid also loses its carboxyl group when heated with a solution containing both sodium hydrogen sulphite and sodium hydroxide; in this case, β-naphthol is produced.

1-Hydroxy-2-naphthoic acid and 2-hydroxy-1-naphthoic acid both very readily lose their carboxyl radicles under these conditions, yielding a naphthylamine in the presence of ammonia and a naphthol under the influence of an alkali hydroxide.

Salicylic acid, on the other hand, is very stable towards hot solutions of the sulphites, and remains unaffected when treated in the manner indicated. G. T. M.

Derivatives of the Nitrophthalic Acids. By HEINRICH SEIDEL and J. C. BITTNER (*Monatsh.*, 1902, **23**, 415—436. Compare Miller, *Annalen*, 1881, **208**, 294).—3-*Nitrophthalimide*, formed when 3-nitrophthalic acid is heated at 220° in a stream of dry ammonia gas, crystallises in yellowish-white needles, melts at 216°, sublimes unchanged, and is easily soluble in alcohol, glacial acetic acid, acetone, or solutions of the alkali hydroxides; it dissolves with difficulty in hot water but is insoluble in the cold solvent; the imide is converted, by Hofmann's reaction, into 6-*nitroanthranilic acid*, melting at 184°, an isomeride of Hübner's 3-nitroanthranilic acid (Abstr., 1879, 380); it has a sweet taste, is easily soluble, and yields a deep orange-red, crystalline, *sodium* salt and a *hydrochloride* crystallising in long, almost colourless, needles. When heated with alcohol and hydrochloric acid, 6-nitroanthranilic acid yields a small amount of *m*-nitroaniline but no ester; when heated with diluted sulphuric acid (1 : 1) at 120°, it is converted into *m*-nitroaniline, and when diazotised and boiled with dilute sulphuric acid it yields *m*-nitrophenol. Reduction by tin and hydrochloric acid leads to the formation of 2 : 6-*diaminobenzoic acid*, the *hydrochloride* of which forms colourless, glistening needles; these become greyish-violet on exposure to light and air, and are easily soluble in alcohol but not in ether. Reduction in presence of excess of hydrochloric acid and rapid evaporation of the liquid leads to the formation of *m*-phenylenediamine.

4-*Nitrophthalimide*, formed at 170° from 4-nitrophthalic acid, crystallises in yellow, glistening leaflets, melts at 202°, sublimes unchanged, has solubilities similar to those of the 6-isomeride, and yields the two possible isomeric nitroanthranilic acids.

5-Nitroanthranilic acid crystallises from dilute alcohol in lemon-yellow, silky needles, melts at 280°, and not at 263° as stated by Hübner (*loc. cit.*), is insoluble in xylene, yields an ethyl ester which melts at 146° (Kaiser, Abstr., 1886, 149) and an acetyl derivative melting at 214—216°; it is converted by diazotisation into 5-nitrosalicylic acid melting at 288° (Hübner, Abstr., 1882, 503; Rupe, Abstr., 1897, i, 416), and reduced by tin and hydrochloric acid to a colourless solution which gives the *p*-phenylenediamine reactions either with aniline hydrochloride and potassium dichromate or with ferric chloride.

4-*Nitroanthranilic acid* [$NH_2 : CO_2H : NO_2 = 2 : 1 : 4$] separates from dilute alcohol as a yellow, crystalline powder having an intensely sweet taste; it is soluble in xylene and forms an orange-red, crystalline *sodium* salt, easily soluble in water, and a *hydrochloride* which crystallises in long, delicate, glistening leaflets and dissociates on drying.

The *ethyl ester*, formed by the action of alcohol and hydrogen chloride, separates from dilute alcohol in clusters of yellow needles melting at 91° and when crystallised from benzene melts at 89°; it has a burning, sweet taste, is insoluble in aqueous sodium carbonate solution, and soluble in benzene. The *acetyl* derivative crystallises in long, slightly yellow needles and melts at 188°. Diazotisation of the 4-acid leads to the formation of 4-*nitrosalicylic acid*, which crystallises in broad, short, orange-yellow needles, melts at 235°, has a bitter taste, is easily soluble in alcohol, chloroform, or benzene, but insoluble in light petroleum, and gives a blood red coloration with ferric chloride. This nitro-compound is reduced by tin and hydrochloric acid to 4-*aminosalicylic acid*, which forms a reddish-brown, crystalline powder, melts at 220°, is easily soluble in water or alcohol, but more sparingly so in ether, forms a *hydrochloride* which is easily oxidised to a dark brown mass on exposure to air, gives an intense dark violet coloration with ferric chloride, and on diazotisation and boiling yields a solution which gives the reactions of 2 : 4-dihydroxybenzoic acid.

Reduction of 4-nitroanthranilic acid by tin and hydrochloric acid leads to the formation of 2 : 4-*diaminobenzoic acid*, which is easily decomposed into carbon dioxide and *m*-phenylenediamine.

G. Y.

Phthalylhydroxylamine. BASLER CHEMISCHE FABRIK (D.R.-P. 130680, 130681).—Phthalylhydroxylamine is produced by the interaction of hydroxylamine hydrochloride and sodium carbonate in aqueous solution on phthalic anhydride, the reagents being present in molecular proportion. When excess of sodium carbonate is added, the intermediate product, *phthalhydroxylamic acid*, $OH\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, may be isolated, being precipitated from the alkaline solution by hydrochloric acid; this substance melts at 204—206° and is readily soluble in alcohol or water; its aqueous solution, when warmed at 50°, yields phthalylhydroxylamine. G. T. M.

Monoacyl Derivatives of Indoxyl and Indoxylic Acid. DANIEL VORLÄNDER & BRUNO DRESCHER (D.R.-P. 131400).—In addition to the results already published (compare Abstr., 1901, i, 563), the following compounds are described for the first time.

3-*Propionylindoxyl*, obtained by treating the decomposition product of phenylglycinecarboxylic acid with propionic acid and propionic anhydride, is insoluble in solutions of the alkali hydroxides and melts at 87°. An isomeride, 1-*propionylindoxyl*, produced by treating indoxyl with propionic anhydride suspended in water, melts at 128° and is soluble in alkalis.

1-*Benzoylindoxyl*, prepared from indoxyl by the Schotten-Baumann reaction, crystallises from dilute acetic acid and melts at 101°; its *nitroso*-derivative crystallises in pale yellow needles and melts at 104°.

3-*Benzoylindoxyl*, resulting from the action of benzoic anhydride on indoxyl at 40°, crystallises from alcohol, melts at 123°, and is soluble in a solution of an alkali hydroxide; its isomeride does not dissolve in this medium.

Sodium acetylindoxylate, formed by the action of acetic anhydride on a slightly alkaline solution of sodium indoxylate, crystallises in lustrous white leaflets containing water of crystallisation. The corresponding salts of calcium and the heavy metals are sparingly soluble in water; the magnesium salt separates in glistening leaflets. G. T. M.

Action of Solid Alkalis on Aromatic Aldehydes. By P. N. RAIKOW and J. RASCHTANOW (*Chem. Centr.*, 1902, i, 1212—1213; from *Oesterr. Chem. Zeit.*, 5, 169—173).—By the action of solid alkali hydroxide on benzaldehyde, *p*-tolylaldehyde, cuminaldehyde, and *o*-chlorobenzaldehyde, theoretical quantities of alcohols and acids are formed. The reaction with benzaldehyde takes place without the formation of any resinous bye-products (compare Meyer, Abstr., 1882, 195). When the chlorobenzaldehydes are similarly treated, the chlorine is divided equally between the two products. *o-Chlorobenzyl alcohol* crystallises in white, lustrous leaflets, melts at 69·5°, and is only very slightly soluble in water, but readily so in alcohol or ether. *p*-Chlorobenzaldehyde is only slowly attacked by alkali; *p*-chlorobenzyl alcohol melts at 71°. Salicylaldehyde, *p*-hydroxybenzaldehyde, and vanillin do not undergo Cannizzaro's reaction with the alkali hydroxides. Anisaldehyde forms anisic acid, which melts at 178·5°. The presence of a hydroxyl group in the ortho- or para-position renders the aldehyde incapable of reacting with alkalis. *o*-Nitrobenzaldehyde yields an acid which decomposes completely at 190—200°, and contains 7·5 per cent. of nitrogen. *p*-Nitrobenzaldehyde and its *m*-isomeride do not form alcohols, but by saturating the products with hydrogen chloride, amorphous substances containing 6 and 8·1 per cent. of nitrogen respectively are obtained. Thus the nitrobenzaldehydes do not yield the normal products, but either form acids with loss of a portion of the nitrogen or compounds in which hydroxyl groups are present in the benzene ring. E. W. W.

α-Substituted Anthraquinone Derivatives containing Chlorine or Bromine. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 131538).—α-Diazoanthraquinone, when treated with hydrochloric or hydrobromic acid, yields the corresponding halogen derivative. In this reaction, the presence of cuprous salts is not essential. G. T. M.

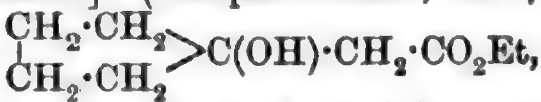
Blue Colouring Matter of the Anthracene Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 129845, 129846, 129847, 129848).—2-Aminoanthraquinone, when melted with potassium hydroxide at 200—300°, yields a leuco-compound which, by aërial oxidation, changes into a pigment closely resembling indigotin; it is insoluble in solutions of the mineral acids or the alkali hydroxides, and crystallises from nitrobenzene in blue needles with a copper-bronze lustre. This *substance*, $C_{14}H_7O_2N$, which may also be obtained from 2-aminohydroxyanthranol, yields a yellow product, and, on oxidation by alkaline reducing agents, is converted into the soluble leuco-derivative.

2-Aminoanthraquinonesulphonic acid, when submitted to fusion with potash at 170—175°, yields the sulphonic acid of the pigment $C_{14}H_7O_2N$, a soluble, blue colouring matter, which may also be obtained by sulphonating the insoluble compound with fuming sulphuric acid, either with or without boric acid.

The *sodium* derivative of the leuco-compound can be isolated in the form of copper-coloured needles by reducing the insoluble colouring matter with a solution of sodium hyposulphite and sodium hydroxide; it dissolves in warm, alkaline solutions, but is readily dissociated by water, regenerating the pigment. G. T. M.

Anthracene Colouring Matters containing Nitrogen. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 127439).—2-Bromo-4-nitro-1-hydroxyanthraquinone is obtained by heating 4-nitro-1-hydroxyanthraquinone-2-sulphonic acid with bromine at 120°; it crystallises from glacial acetic acid in lustrous, yellow needles, dissolving in concentrated sulphuric acid to a light yellow solution which becomes reddish-yellow on the addition of boric acid. When heated with primary aromatic amines, it yields blue colouring matters. By the action of *p*-toluidine, for example, the nitro-group is replaced by the tolylamino-radicle and a substance is obtained identical with that produced by condensing this amine with 2 : 4-dibromo-1-hydroxyanthraquinone. When boric acid is added during the fusion, the colouring matters are green. G. T. M.

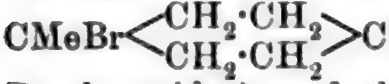
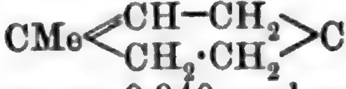
Preparation of Ionone. HAARMANN & REIMER (D.R.-P. 129027).—ψ-Ionone, when treated with warm dilute mineral acids, always yields α-ionone mixed with varying quantities of its β-isomeride. The latter compound is formed almost exclusively when the transformation is induced by 70 to 100 per cent. sulphuric acid in the cold, whereas α-ionone containing only traces of the isomeric compound is produced when the reaction is carried out with concentrated phosphoric acid at 30° (compare Abstr., 1901, i, 157; this vol., i, 342, 471).
G. T. M.

New Syntheses in the Terpene Series. By OTTO WALLACH (*Chem. Centr.*, 1902, i, 1293—1296; from *Nachr. k. Ges. Wiss. Göttingen*, 1902, 92—107). [With NICOLAI SPERANSKI.] (Compare Abstr., 1901, i, 155).—*Ethyl* cyclo*pentanolacetate*,  $\begin{array}{l}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{array}\!>C(OH)\cdot CH_2\cdot CO_2Et$, produced by the influence of zinc on *cyclo*pentanone and ethyl bromoacetate, boils at 105—107° under 11 mm. pressure. By the elimination of water, it forms an unsaturated *ester*, $C_9H_{14}O_2$, which boils at 82—84° under 11 mm. pressure. The corresponding *acid*, $C_7H_{10}O_2$, melts at 49—50° and boils at 122° under 11 mm. pressure; the *dibromide*, $C_7H_{10}Br_2O_2$, melts at 88°, and the *amide*, $C_6H_9\cdot CO\cdot NH_2$, at 144°. The unsaturated *ester*, $C_{10}H_{16}O_2$, derived from ethyl β-methyl*cyclo*pentanolacetate, boils at 90—92° under 11 mm. pressure; its *acid*, $C_8H_{12}O_2$, boils at 128° under 10 mm. pressure or about 240° under the ordinary pressure with liberation of carbon dioxide. The *nitrile*, $C_7H_{11}\cdot CN$, boils at 208—210°. The *amide*, $C_7H_{11}\cdot CO\cdot NH_2$, melting at 128°, together with a *hydrocarbon*, C_7H_{12}, is prepared by heating the ammonium salt of the unsaturated acid at 230°. The hydrocarbon boils at 96—97° and has a sp. gr. 0·7750 and n_D 1·4336 at 16°.

Similarly, by means of the ethyl bromoacetate synthesis, from dihydrocarvone and carvenone on the one hand and menthone and tetrahydrocarvone on the other, unsaturated acids can be obtained which decompose with liberation of carbon dioxide and formation of homoterpenes, $C_{11}H_{18}$, and homomenthenes, $C_{11}H_{20}$.

[With FRITZ THÖLKE.]—The *terpene*, $C_{11}H_{18}$, prepared from dihydrocarvone, boils at 191—192° and has a sp. gr. 0·8465 and n_D 1·4771. The unsaturated *ester*, $C_{10}H_{15}\cdot CH_2\cdot CO_2Et$, from which it is derived, boils at 145—148° under 18 mm. pressure. The *terpene*, $C_{11}H_{18}$, obtained from carvenone, boils at 194—197° and has a sp. gr. 0·8510 and n_D 1·4821. The unsaturated *ester*, $C_{10}H_{15}\cdot CH_2\cdot CO_2Et$, boils at 135—137° under 16 mm. pressure. *Menthene*, $C_{11}H_{20}$, prepared from menthone, boils at 196—197° and has a sp. gr. 0·8215 and n_D 1·4579. The isomeric *menthene*, $C_{11}H_{20}$, from tetrahydrocarvone, boils at 194—195° and has a sp. gr. 0·8300 and n_D 1·4619.

II. [With NICOLAI SPERANSKI.]—In order to distinguish between α- and β-adipic acids, the methylpentanones obtained by distilling the calcium salts are condensed with benzaldehyde. α-Methylpentanone yields a *monobenzylidene* derivative, $C_5H_8O\colon C\colon CHPh$, which crystallises in colourless needles and melts at 123—124°, whilst β-methylpentanone forms dibenzylidene-β-methylpentanone melting at 149—151°. By means of this condensation, the acid obtained by oxidation of pulegone and methylhexanone has been proved to be β-methyladipic acid (compare Markownikoff, Abstr., 1900, i, 475). When β-methyladipic acid is distilled in a vacuum, it is partially converted into the anhydride; only a portion of the distillate is soluble in dry benzene and melts at 84°, whilst the insoluble residue melts at 91°.

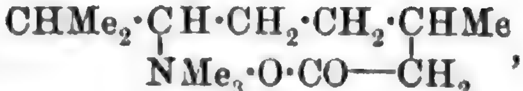
III. [With O. RAHN.]—When the terpineol (m. p. 32°) discovered by Helle and Stephan in liquid terpineol (compare Schimmel & Co., Abstr., 1901, i, 394) is treated with bromine and a solution of hydrogen bromide in glacial acetic acid, a *terpineol tribromide*,  $\mathrm{CMeBr}{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}\mathrm{CH\cdot CMeBr\cdot CH_2Br}$, is formed which melts at 65°. By the oxidation of this compound with potassium permanganate, a *trihydroxy*-derivative, $C_{10}H_{20}O_3$, is obtained. This compound crystallises from ethyl acetate, melts at 116—117°, and when boiled with dilute sulphuric acid loses water and forms the compound $C_{10}H_{16}O$, which boils at 217—225° under atmospheric pressure, has a sp. gr. 0·977, n_D 1·4930 at 20°, and is analogous to the isomeric compound prepared from the oxidation product, $C_{10}H_{20}O_3$, of dihydrocarveol. By warming the oxyketone, $C_9H_{16}O_2$, prepared by Helle and Stephan (*loc. cit.*), with dilute sulphuric acid or by oxidising the trihydroxyterpineol with chromic acid, *tetrahydro-p-tolyl methyl ketone*,  $\mathrm{CMe}{<}\genfrac{}{}{0pt}{}{CH-CH_2}{CH_2\cdot CH_2}{>}\mathrm{CH\cdot COMe}$, is formed; it boils at 205—206°, has a sp. gr. 0·940, and n_D 1·4719 at 19°, and when heated with sulphuric acid (4 vols.) yields *p*-tolyl methyl ketone. The *semicarbazone* of tetrahydro-*p*-tolyl methyl ketone melts at 164—165°. The *oxime* crystallises from dilute alcohol, melts at 51—52°, and is readily soluble in light petroleum. The *dibromo-oxime*, $C_9H_{14}Br_2\colon NOH$, melts at 130°. The secondary *alcohol*, $C_9H_{16}O$, prepared by the action of sodium on an alcoholic or ethereal solution of the ketone, is a lower homologue of the terpineol melting at 35°; it boils at 212—213°, has a sp. gr. 0·942, and n_D 1·4836 at 19°.

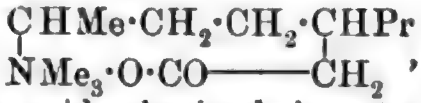
When the oxylactone, $C_{10}H_{16}O_3$, prepared by oxidising pulegenic acid with potassium permanganate, is treated with a small quantity of concentrated sulphuric acid, the ketone *pulenone*, $C_9H_{16}O$, is formed which boils at 183° and has a sp. gr. 0·8925 and n_D 1·44506 at 21°. *Pulenol*, $C_9H_{18}O$, obtained by reducing pulenone, boils at 187—189°, has a sp. gr. 0·8953, and n_D 1·4569 at 20°; by the elimination of water it forms pulenene, C_9H_{16}. *Pulenene nitrosochloride*, $C_9H_{16}\cdot NOCl$, is a blue substance melting at 88—89°. *Pulenoneoxime*, $C_9H_{16}\colon NOH$, melts at 94—95°; *pulenoneisooxime* melts at 96—97° and by the action of acids forms nonylenic acid. Both oximes are easily converted into the nitrile of nonylenic acid, which boils at 216—217°.

[With Colmann.]—*Pulegene*, C_9H_{16}, prepared by eliminating carbon dioxide from pulegenic acid, boils at 138—139°, has a sp. gr. 0·791, n_D 1·44, and on oxidation yields a ketonic *acid*, $C_9H_{16}O_3$, which boils at 265° or at 164° under 15 mm. pressure. The *semicarbazone* melts at 164° and *pulegene nitrosochloride*, $C_9H_{16}\cdot NOCl$, is a readily soluble, white substance.

[With Thede.]—*Pulegene nitrolepiperidide*, $C_9H_{16}ON\cdot C_5NH_{10}$, melts at 106—107°. By elimination of hydrogen chloride from the nitrosochloride, *pulegenoneoxime*, $C_9H_{14}\colon NOH$, a liquid boiling at 120—125° under 11 mm. pressure, is formed, and by the action of acids on this compound *pulegenone*, $C_9H_{14}O$, is obtained. The latter boils at 189—190° and has a sp. gr. 0·914 and n_D 1·4645. The *alcohol*, $C_9H_{18}O$, prepared by reducing pulegenone, boils at 77—78° under 15 mm. pressure and on oxidation yields *dihydropulegenone*, $C_9H_{16}O$, which boils at 188—189°, has a sp. gr. 0·889, and n_D 1·4439 at 20° and is not attacked by cold potassium permanganate. The *semicarbazone* melts at 176—178° and is very slightly soluble in alcohol. The *oxime* does not readily solidify.

[With A. Scheunert.]—cyclo-*Geraniolene* resembles pulegene, boils at 138—139°, and has a sp. gr. 0·8030 and n_D 1·44406. The *nitrosochloride*, $C_9H_{16}\cdot NOCl$, and *nitrosate*, $C_9H_{16}N_2O_4$, have been prepared. The *nitrolepiperidide*, $C_9H_{16}ON\cdot C_5NH_{10}$, melts at 136—138° and the *nitrolebenzylamine*, $C_9H_{16}ON\cdot NH\cdot C_7H_7$, at 106°. By boiling with alcoholic potassium hydroxide, the nitrosochloride and nitrosate form *trimethyl*cyclo*hexenoneoxime*, $C_9H_{14}\colon NOH$, which crystallises from ether or light petroleum, melts at 128—129°, boils at 131—132° under 15 mm. pressure, and by the action of acids forms *trimethyl*cyclo*hexenone*, $C_9H_{14}O$. The latter compound boils at 195—196°, has a sp. gr. 0·9245, and n_D 1·4749 at 25°, and appears to exist only in the enolic form. The *semicarbazone* melts at 158—159° and is rather soluble in cold ether. By the action of sodium and alcohol on hexenone, a *pinacone* melting at 128—130° and *trimethyl*cyclo*hexanol*, $C_9H_{18}O$, are formed. The latter is an oil, has the odour of camphor, boils at 192—193°, and on oxidation yields *trimethyl*cyclo*hexanone*, $C_9H_{16}O$, which boils at 191° and has a sp. gr. 0·9 and n_D 1·4548; the *oxime* melts at 108—109°.

IV. [With Kösch.]—By the action of methyl iodide on the ethyl ester of aminodecoic acid obtained from menthoneisooxime (Abstr., 1900, i, 589), a quaternary *iodide*, $C_9H_{18}NMe_3I\cdot CO_2Et$, melting at 117°, is formed, and by treating the chloride prepared from this compound with silver oxide, an ε-*betaine*,  $\begin{array}{l}\mathrm{CHMe_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe}\\ \qquad\quad\mathrm{NMe_3{\cdot}O{\cdot}CO{-}CH_2}\end{array}$, is obtained. The *hydrochloride* melts at 191—192°.

[With L. FRESENIUS.]—An isomeric *betaine*,  $\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CHPr}\\ \mathrm{NMe_3{\cdot}O{\cdot}CO{-\!\!-\!\!-}CH_2}\end{array}$, may also be prepared from the aminodecoic acid obtained by the decomposition of tetrahydrocarvone*iso*oxime.

V. [With BÖCKER.]—By the reduction of phellandrene nitrite, prepared from water-fennel oil by Pesci's method with zinc and glacial acetic acid (*Gazzetta*, 1886, **16**, 229), a lævorotatory diamine is obtained which boils at 250—253°, but resembles Pesci's diamine (b. p. 209—214°) in every other property. When phellandrene nitrite from *Eucalyptus amygdalina* is simply reduced, a lævorotatory *diamine* which is not identical with Pesci's is formed. It boils at 250—253° or at 132—134° under 17 mm. pressure, and is not readily volatile in steam. The *hydrochloride*, $C_{10}H_{16}(NH_2)_2,HCl$, or $C_{10}H_{18}(NH_2)_2,HCl$, melts at 209—210°, is not affected by exposure to air, is slightly soluble in cold alcohol, and on dry distillation yields cymene, ammonia, and ammonium chloride. The *platinichloride* is readily soluble in water. The phellandrenes obtained from different sources cannot, therefore, be identical, and the earlier formula for the nitrite containing the group $\mathrm{NO{\cdot}\dot{C}H{\cdot}\dot{C}HO{\cdot}NO}$ requires modification. E. W. W.

Double Glucoside of Frangula Bark. By E. AWENG (*Chem. Centr.*, 1902, ii, 147; from *Apoth. Zeit.*, **17**, 372—373. Compare Abstr., 1901, i, 39).—The original paper contains a detailed description of the preparation of the double glucoside of frangula bark in a state of purity, together with an account of its decomposition products and its relationship to ψ-frangulin and frangulic acid.

E. W. W.

Theory of the Dyeing Process. By P. D. ZACHARIAS (*Chem. Zeit.*, 1902, **26**, 680—681. Compare this vol., i, 635).—The dyeing process is governed by two phases: absorption and fixation. The colloidal nature of the fibre and the catalytic influence of the fibre on the formation of a colloidal precipitate must be taken into account. The equation given by Wegscheider (this vol., i, 635) should be $dc/dx = d(c_1^{\nu})/dx = 0$, in the integration of the formula developed from Fick's law. The value of ν may be greater than, equal to, or less than unity. J. McC.

***allo*Cinchonine.** By ARPÁD VON PECSICS (*Monatsh.*, 1902, **23**, 443—454. Compare Hlavnička, Abstr., 1901, i, 404).—When boiled with acetic anhydride, *allo*cinchonine forms an *acetyl* derivative, which crystallises from light petroleum in white plates, sinters at 88°, melts at 92—94°, is easily soluble in alcohol, ether, benzene, or chloroform, and yields *allo*cinchonine when hydrolysed by alcoholic potassium hydroxide. *Benzoyl*allo*cinchonine hydrochloride*, formed from *allo*cinchonine and benzoyl chloride, is an amorphous powder; it melts at 230°, crystallises either from water in plates or from dilute alcohol in prisms which lose $2H_2O$ at 105° and melt at 223°. The *benzoyl* derivative crystallises from ether in short, white needles, melts at 118—119° and is hydrolysed by alcoholic potassium hydroxide to *allo*cinchonine and benzoic acid. When acted on by phosphorus pentachloride in chloroform solution, *allo*cinchonine yields *allo-cinchonine chloride*, $C_{19}H_{21}N_2Cl$. These reactions distinguish *allo*cinchonine from *a*- and *β*-*iso*cinchonine, these bases giving negative results in the preceding experiments. These differences may be explained by assuming that *allo*cinchonine contains a reactive hydroxyl group which is either absent in the molecules of its isomerides or marked by a different spacial configuration. With methyl iodide, *allo*cinchonine forms a *methiodide*, $C_{19}H_{22}ON_2,MeI,\frac{1}{2}H_2O$, which crystallises in clusters of white needles, melts and decomposes at 245°, is easily soluble in hot water or ethyl alcohol, and sparingly so in methyl alcohol, and a *dimethiodide*, $C_{19}H_{22}ON_2,2MeI,2H_2O$, which crystallises in red needles or large, garnet-red monoclinic crystals, loses $2H_2O$ at 105°, and melts at 235°. The methiodide forms a *hydriodide*, $C_{19}H_{22}ON_2,MeI,HI$, which crystallises in clusters of yellow plates, contains no water of crystallisation, and melts at about 232°, is easily soluble in hot water or alcohol, sparingly so in cold water or methyl alcohol, and gives a white, crystalline product on treatment with warm sodium carbonate solution.

allo*Cinchonine hydriodide*, $C_{19}H_{22}ON_2,HI,H_2O$, crystallises in white prisms, is easily soluble in ethyl alcohol, sparingly so in methyl alcohol, and forms with methyl iodide a second *methiodide hydriodide*, $C_{19}H_{22}ON_2,MeI,HI,\frac{1}{2}H_2O$, which crystallises in glistening, lemon-yellow needles, loses $\frac{1}{2}H_2O$ at 105°, melts at 250—253°, is easily soluble in ethyl alcohol, sparingly so in methyl alcohol, insoluble in ether, and on treatment with warm sodium carbonate solution yields a red, amorphous substance insoluble in ether. *allo*Cinchonine must therefore be a di-tertiary base. G. Y.

_allo_Cinchonine. By Zdenko Hanns Skraup and Rud. Zwerger (*Monatsh.*, 1902, **23**, 455—468. Compare preceding abstract).—*allo*Cinchonine sulphate is oxidised by chromic acid to carbon dioxide, formic acid, acetic acid, cinchonic acid, kynurine, and allo*meroquinenine*; the last of these forms a *platinichloride*, $(C_9H_{15}O_2N)_2,H_2PtCl_6,3H_2O$, crystallising from water in microscopic prisms which lose $3H_2O$ at 110° and melt at 210—211°; a *hydrochloride*, which crystallises in clusters of needles, has a sp. gr. 1·0175, and $[a]_D$ $-114°$, and an *aurichloride*, $C_9H_{15}O_2N,HAuCl_4$, which crystallises in delicate needles, melts at 165—166°, is soluble in warm water, and is partly decomposed by boiling water.

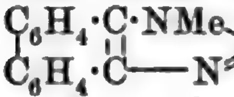
*allo*Meroquinenine is isomeric with meroquinenine and with *β*-*iso*meroquinenine obtained by oxidation from cinchonine and also from *β*-*iso*cinchonine. When heated with lime, it gives the same odour as is observed on similar treatment of cincholeuponic acid, cincholeupon, and *β*-*iso*meroquinenine, and when heated with zinc dust an oil having an odour resembling that of pyridine. The molecule of *allo*cinchonine contains a quinoline nucleus and the remainder must be constituted similarly to that of cinchonine.

Cincholeuponic acid is not formed in the oxidation of *allo*cinchonine, as the part of the product insoluble in alcohol does not form an optically active hydrochloride.

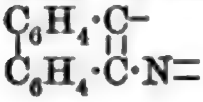
On oxidation by potassium permanganate, *allo*cinchonine sulphate yields formic acid and an amorphous substance resembling cinchotenine.

Cinchonine and *allo*cinchonine in sulphuric acid solution decolorise potassium permanganate, at first rapidly, the rate of oxidation gradually decreasing; with α- and β-*iso*cinchonine, the action is at first slow, increases in rapidity, and is accompanied by much frothing. α- and β-*iso*Cinchonine are probably stereoisomerides of cinchonine and *allo*cinchonine. G. Y.

Correlation of the Constitution and Physiological Action of Morphine. By Ernst Vahlen (*Chem. Centr.*, 1902, i, 1302—1303; from *Arch. exp. Path. Pharm.*, **47**, 368—410).—Since epiosine,

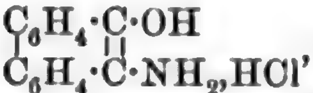


$\begin{matrix} C_6H_4\cdot C\cdot NMe \\ \| \\ C_6H_4\cdot C\text{——}N \end{matrix}{>}CH$, has been found to possess physiological properties similar to those of morphine, the pharmacological action of the latter must be dependent on the presence of the phenanthrenoid group,



$\begin{matrix} C_6H_4\cdot C- \\ \| \\ C_6H_4\cdot C\cdot N{=} \end{matrix}$.

Morphigenine hydrochloride,



$\begin{matrix} C_6H_4\cdot C\cdot OH \\ \| \\ C_6H_4\cdot C\cdot NH_2,HCl \end{matrix}$, prepared by reducing phenanthraquinone hydrazone with stannous chloride, crystallises in coloured needles, becomes reddish at 180°, but does not melt at 290°, is decomposed by water, especially on heating, and is readily soluble in boiling glacial acetic acid or in hot concentrated hydrochloric acid, but only slightly so in the cold solvents. By the action of alkali hydroxides or carbonates on the hydrochloride, phenanthraquinone is regenerated. By the action of zinc chloride on morphigenine hydrochloride, products were obtained which were not isolated, but their aqueous solutions had a distinct narcotic effect on dogs and frogs. Epiosine, prepared by the action of methylamine on morphigenine hydrochloride, was found to be identical with Japp and Davison's *N*-methylphenyleneimidazole (Trans., 1895, **67**, 32); it melts at 195°. The physiological actions of morphigenine hydrochloride and epiosine are described in detail in the original paper. E. W. W.

2-Cyanopyridine. By Hans Meyer (*Monatsh.*, 1902, **23**, 437—442. Compare Abstr., 1901, i, 407).—Picolinamide is best prepared by the action of aqueous ammonia on picolinyl chloride and extraction with chloroform. In the preparation of the amide from the ester, the solution of the hydrochloride from the latter, obtained by passing hydrogen chloride into an absolute alcoholic solution of picolinic acid, is concentrated and shaken with aqueous ammonia (compare Abstr., 1894, i, 425, 472).

2-*Cyanopyridine*, prepared by the action of thionyl chloride on picolinamide at 90—100°, crystallises from ether in long, colourless needles, melts at 26°, is slightly volatile at the ordinary temperature, boils at 212—215°, has an intense odour resembling those of benzaldehyde and of coumarin, and is easily soluble in water, alcohol, ether, or chloroform. It has slight basic properties and forms an orange-red, crystalline *platinichloride*, $(C_6H_4N_2)_2,H_2PtCl_6$, and an *aurichloride*, $C_6H_4N_2,HAuCl_4$, which crystallises in lemon-yellow needles, losing about $1H_2O$ and becoming opaque at 100°; it melts at 190° and is sparingly soluble in water, dissolving easily in dilute hydrochloric acid.

Picolinic acid forms an *aurichloride* which crystallises in glistening, straw-yellow leaflets, melts at 200°, decomposes with evolution of gas at 204°, and is easily soluble in water.

Picolinamide aurichloride is an insoluble, light yellow, crystalline powder which sinters at about 215°, but melts only at a much higher temperature. The *aurichloride* of 2-aminopyridine crystallises from concentrated hydrochloric acid in long, glistening, garnet-red needles and melts at 231°. 2-Cyanopyridine is hydrolysed by concentrated hydrochloric acid at 120°, giving a quantitative yield of ammonia and picolinic acid. G. Y.

Tetra-aquodipyridinechromium Salts. By PAUL PFEIFFER (*Zeit. anorg. Chem.*, 1902, **31**, 401—436).—Werner's theory connecting the metal-ammonia compounds and salt hydrates is supported by the facts now known about the intermediate products. The author has investigated some of these intermediate products containing pyridine in place of ammonia. [In the formulæ given $Py = C_5NH_5$.]

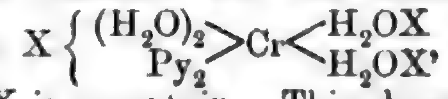
The chloride, $CrCl_3,2Py,6H_2O$, loses 2 mols. of water in a desiccator containing phosphoric oxide and gives $CrCl_3,2Py,4H_2O$; therefore, according to Werner's theory, it is to be regarded as

$$[CrPy_2(H_2O)_4]Cl_3,2H_2O,$$

and is consequently an intermediate product between $[CrPy_6]Cl_3$ and $[Cr(H_2O)_6]Cl_3$. In aqueous solution, all the chlorine is ionised and it undergoes metathetical reactions. Like the pure hydrates, it gives basic salts such as $[CrPy_2(H_2O)_2(OH)_2]Cl$ when hydroxides are added. The salts are all red, crystallise well from water, and the aqueous solutions have an acid reaction. When heated, they give off pyridine and become green. The basic salts dissolve in acids, giving red solutions. It has not been possible to prepare the free base,

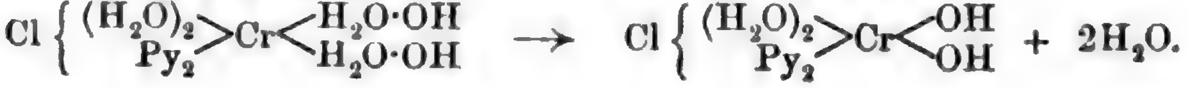
$$[CrPy_2(H_2O)(OH)_3],$$

because the basic salts dissolve in alkalis or ammonia.

The author has already introduced a slight modification (*Naturwiss. Rundsch.*, 1901, 366) into Werner's theory. According to the proposition suggested, a definite place in the molecule is assigned to the negative radicle. For the tetra-aquodipyridinechromium salts, the formula  $X\left\{\begin{matrix}(H_2O)_2\\Py_2\end{matrix}\right.>Cr<\begin{matrix}H_2OX\\H_2OX\end{matrix}$, is given, indicating that the position of one X is uncertain. This shows that these are oxonium salts. The properties of the hydroxylopyridine salts which have been obtained indicate that they are not the basic salts corresponding with

$$[CrPy_2(H_2O)_4]X_3;$$

they are rather to be regarded as salts of pseudo-bases formed from the true bases by splitting off of water:

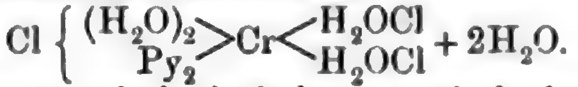


$$Cl\left\{\begin{matrix}(H_2O)_2\\Py_2\end{matrix}\right.>Cr<\begin{matrix}H_2O\cdot OH\\H_2O\cdot OH\end{matrix} \rightarrow Cl\left\{\begin{matrix}(H_2O)_2\\Py_2\end{matrix}\right.>Cr<\begin{matrix}OH\\OH\end{matrix} + 2H_2O.$$

The idea of pseudo-salts can also be advantageously applied to metal-ammonia compounds.

The starting point for the preparation of the tetra-aquodipyridinechromium salts is *diaquodihydroxylodipyridinechromium chloride*, $[CrPy_2(OH)_2(H_2O)_2]Cl$, which is obtained from green chromic chloride hexahydrate, $[Cr(H_2O)_4Cl_2]Cl,2H_2O$, by the action of pyridine; it may be prepared in like manner from the double salt, $[Cr(H_2O)_3Cl_3],2HClPy$, which is most easily obtained by adding successively pyridine and a large excess of concentrated hydrochloric acid to a solution of chromic chloride; a third method of preparation is by warming $CrCl_3Py_3$ with a 10 per cent. solution of ethylenediamine. The diaquo-salt is obtained in fine needles which decompose at 100°; it is quite insoluble in the ordinary solvents, but can be recrystallised from pyridine.

When the dihydroxylochloride is treated with concentrated hydrochloric acid, the greenish-grey compound is converted into a red, crystalline mass of *tetra-aquodipyridinechromium chloride*,



$$[CrPy_2(H_2O)_4]Cl_3,2H_2O \text{ or } Cl\left\{\begin{matrix}(H_2O)_2\\Py_2\end{matrix}\!\!>\!Cr\!<\!\!\begin{matrix}H_2OCl\\H_2OCl\end{matrix}\right. + 2H_2O.$$

This is very easily soluble in water, ethyl alcohol, or methyl alcohol, but insoluble in ether, acetonitrile, acetic acetate, acetic acid, or chloroform. The aqueous solution remains unchanged at the ordinary temperature, but decomposition occurs when it is heated on the water-bath. The red, alcoholic solution quickly decomposes and deposits the greenish, basic chloride. The reactions with various reagents have been studied. In the air, the salt is converted into the greenish-violet *hydroxylotriaquodipyridinechromium chloride*, $[CrPy_2(H_2O)_3OH]Cl_2$.

Tetra-aquodipyridinechromium bromide, $[CrPy_2(H_2O)_4]Br_3,2H_2O$, obtained from the dihydroxylochloride, or the normal chloride, by solution in concentrated hydrobromic acid, separates in red crystals from concentrated hydrobromic acid solution. It closely resembles the chloride but is rather more stable. *Dihydroxylodiaquodipyridinechromium bromide*, $[CrPy_2(H_2O)_2(OH)_2]Br$, is almost quantitatively precipitated by the addition of pyridine to a solution of the normal bromide; it has a greenish tinge and is decomposed on heating.

When the dihydroxylochloride is rubbed with sulphuric acid, a red solution is produced from which flat, red needles of *tetra-aquodipyridinechromium hydrogen sulphate*, $SO_4[CrPy_2(H_2O)_4]SO_4H,2H_2O$, separate. The salt is very easily soluble in water and the solution has an acid reaction; it is insoluble in alcohol or ether. When alcohol is added to the concentrated aqueous solution of this salt, violet crystals of *tetra-aquodipyridinechromium sulphate*,

$$[CrPy_2(H_2O)_4]_2(SO_4)_3,3H_2O,$$

are formed. This sulphate remains unchanged in the air, but is decomposed by water; when placed beside phosphoric oxide, it does not lose in weight. When a solution of the tetra-aquo hydrogen sulphate is precipitated with pyridine, fine, greyish-blue crystals of *hydroxylotriaquodipyridinechromium sulphate*, $[CrPy_2(H_2O)_3(OH)]SO_4$, separate; the latter salt is soluble in much water to a greenish solution having a neutral reaction.

Tetra-aquodipyridinechromium chromicyanide,

$$[CrPy_2(H_2O)_4]Cr(CN)_6,2H_2O,$$

is precipitated when potassium chromicyanide is added to a solution of the tetra-aquochloride containing some hydrochloric acid. It is obtained in red plates which are insoluble in water. J. McC.

Hydroxypyrazolone Derivatives of the Naphthalene Series. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 131537).—The hydrazine derivative obtained from 7-amino-α-naphthol-3-sulphonic acid, when condensed with ethyl acetoacetate in the presence of dilute acetic acid, gives rise to hydroxypyrazolonesulphonic acid, which separates in granular crystals when the mixture is treated with excess of hydrochloric acid. This product yields a yellow *nitroso*-derivative.

Other hydrazines of the naphthalene series may be employed in this condensation and the reaction also occurs with ethyl oxaloacetate or dihydroxytartaric acid. G. T. M.

Chloro-*m*-phenylenediaminecarboxylic Acid. By PAUL COHN and MARKUS SCHIFFERES (*Chem. Centr.*, 1902, i, 1293; from *Zeit. Farben- Textil-Chem.*, 1902, 1, 205—206).—4-*Chloro*-m-*phenylenediamine-5-carboxylic acid* or 2-*chloro*-3 : 5-*diamino*-1-*benzoic acid*,

$$C_6H_2Cl(NH_2)_2\cdot CO_2H,$$

prepared by reducing 2-chloro-3 : 5-dinitrobenzoic acid with stannous chloride and hydrochloric acid, is very readily soluble in water and was not isolated. The *hydrochloride*, $C_7H_7O_2N_2Cl,2HCl$, crystallises from alcohol in small, pale yellow needles. The *sulphate*,

$$C_7H_7O_2N_2Cl,H_2SO_4,H_2O,$$

was also prepared. The *diacetyl* derivative, $C_6H_2Cl(NHAc)_2\cdot CO_2H$, crystallises from water in needles and melts at 288—289°. 2-Amino-3 : 5-dinitrobenzoic acid, on reduction with stannous chloride and hydrochloric acid, forms 2 : 3 : 5-triaminobenzoic acid. The free acid prepared by treating the solution of the hydrochloride,

$$C_7H_9O_2N_3,3HCl,$$

with sodium acetate quickly becomes red. The sulphate forms brownish-yellow needles and is almost insoluble in water. E. W. W.

3-Amino-4-methylpheno-β-naphthacridine. FRITZ ULLMAN (D.R.-P. 130943).—3-*Amino-4-methylpheno-β-naphthacridine*, formerly obtained by condensing 2 : 4 : 2′ : 4′-tetra-amino-3 : 3′-ditolylmethane with β-naphthol, is now prepared by heating the latter compound at 200° with the product, $C_8H_{10}N_2$, formed by the interaction of formaldehyde and tolylene-2 : 4-diamine in molecular proportion, the reaction being effected in neutral solutions. G. T. M.

Proteids of Yeast. By R. SCHRÖDER (*Beitr. chem. Physiol. Path.*, 1902, 2, 389—403).—The proteid substance, which can be obtained from yeast by treatment with ether and water, and can be precipitated from this solution by heating, gives all the proteid reactions; the lead reaction is feeble. By decomposition with acids, it yields leucine, tyrosine, phenylalanine, and bases. The bases contain about a quarter of its total nitrogen, and of them lysine is the most abundant. A part of the sulphur is present in a cystin-like combination. The question of a carbohydrate group is left for future consideration.

W. D. H.

Melanins which Originate from Proteid. By FRANZ SAMUELY (*Beitr. chem. Physiol. Path.*, 1902, **2**, 355—388).—The ill characterised and probably numerous substances, named melanins and melanoidins, can be artificially prepared from proteids. In their formation, the tyrosine group, and especially the heterocyclic nucleus (pyrrole, pyridine, skatole) of the proteid appears to be important. The relationship of these substances to humin is discussed. W. D. H.

The Albumose Precipitates produced by Papain and Rennin (Coaguloses and Plasteins). By D. KURAÉEFF (*Beitr. chem. Physiol. Path.*, 1902, **2**, 411—424).—The precipitates produced by adding rennin and papain to various albumoses and caseoses were examined and analysed. These substances are probably closely related to anti-albumid, and possibly to bacterial coagulins. These are characterised by a high percentage of carbon and a low percentage of nitrogen, so differing from the proteoses. W. D. H.

Decomposition of Proteids. By H. STEUDEL (*Zeit. physiol. Chem.*, 1902, **35**, 540—544).—The usual method of obtaining hexon bases from proteids is by means of mineral acid. If boiling baryta water is used instead, the proportion of the bases is different, lysine being by far the most abundant. Whether this is due to the destruction of the other bases during the boiling is uncertain. The decomposition of proteids produced by ferments is very similar to that produced by baryta. W. D. H.

The Nucleo-proteid of the Suprarenal Gland. By WALTER JONES and G. H. WHIPPLE (*Amer. J. Physiol.*, 1902, **7**, 423—434).—This substance is not a nucleo-histon, and its composition is identical whether prepared from the ox or sheep. It is closely similar to that obtained from the pancreas. On decomposition, it yields guanine and adenine in the same relative proportion. Xanthine, hypoxanthine, and epiguanine are either absent or present in the merest traces. As these three bases were found by Okerblom (Abstr., 1899, ii, 778) in suprarenal extracts, there is an interesting and curious difference between the bases preformed in the gland and those which result from the hydrolytic decomposition of its nucleo-proteid. W. D. H.

The Constitution of Proteid Cystin. By ERNST FRIEDMANN (*Beitr. chem. Physiol. Path.*, 1902, **2**, 433—434).—The older physiologists regarded the sulphur-containing complex in a proteid as the source of taurine. Recent research has shown that the sulphur-group of proteid is cystin or cystein. The possibility of its transformation into taurine is excluded if Baumann is correct in considering that cystein is α-aminothiolactic acid, $SH\cdot CMe(NH_2)\cdot CO_2H$.

The present research shows that the cystin from proteid is different from ordinary cystin. Proteid cystein is a compound of β-thiolactic acid, $SH\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$. By the usual treatment, this can be changed into cysteic acid (aminosulphopropionic acid), $SO_3H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, and from this, by the loss of carbon dioxide, taurine, $SO_3H\cdot CH_2\cdot CH_2\cdot NH_2$, is obtained.

Proteid cystein is thus a derivative of glyceric acid, not, as with mercapturic acid cystein, of pyruvic acid, and stands in close relationship to serin. W. D. H.

Action of Iodine on Proteids. I. By C. H. L. Schmidt (*Zeit. physiol. Chem.*, 1902, **35**, 386—395. Compare this vol., i, 251).—The amount of amic nitrogen eliminated from the proteid molecule during iodination is a function of the concentration of the iodine solution used; the more concentrated the solution, the greater is the amount of iodide and iodate formed and the less that of hydriodic acid.

J. J. S.

Experiments on Malt Diastase. By Arthur R. Ling and Bernard F. Davis (*J. Fed. Inst. Brewing*, 1902, **8**, 475—495).—When diastase from well-grown, low-dried malt is allowed to act on starch paste of 2—5 per cent. strength at 50—60°, the starch is hydrolysed in about 1½ hours to a point at which $[\alpha]_{D\ 3\cdot 93}$ is 149·5—150° and the cupric reducing power $R_{3\cdot 93}$ is 77—78, whilst after 42 hours these constants are substantially those of maltose, and in such a solution nothing but maltose can be detected. Diastase prepared from malt grown under abnormal conditions (such as small quantities prepared in the laboratory) and diastase which has been slowly heated to 115—120° do not hydrolyse the starch completely to maltose, even if allowed to act in large excess; diastase which has been rapidly heated to 115—120° produces a more pronounced effect.

Neither the final temperature at which a sample of malt has been kilned (considered alone), nor the "diastatic power" determined in accordance with Kjeldahl's "law of proportionality" by Lintner's method, is a criterion of its behaviour towards starch. When a diastase solution is heated above 65°, its reaction with starch paste appears to be quite different to that of a solution which has not been heated above 60°; this is shown, not only by the specific rotatory and cupric reducing power of the dissolved matter, but also by the presence of dextrose among the final products of hydrolysis. E. G.

Catalase. By Oscar Loew (*Zeit. Biol.*, 1902, **43**, 256—257).—The ferment in milk which causes decomposition of hydrogen peroxide has been termed superoxydase by Raudnitz. It is identical with the ferment previously named catalase by the author (Abstr., 1901, i, 435). W. D. H.

Organic Chemistry.

Composition of Petroleum. Hydrocarbons in Pennsylvania Petroleum with Boiling Points above 216°. By CHARLES F. MABERY (*Amer. Chem. J.*, 1902, **28**, 165—198).—The following hydrocarbons have been isolated from the fractions of Pennsylvania petroleum boiling above 216°; they were purified by treatment with fuming sulphuric acid.

Tridecane, $C_{13}H_{28}$, boils at 221—222° and has a sp. gr. 0·7834 and n_D 1·4354 at 20°; its *chloro*-derivative, $C_{13}H_{27}Cl$, boils at 135—140° under 12 mm. pressure and has a sp. gr. 0·8973 and n_D 1·451 at 20°.

Tetradecane, $C_{14}H_{30}$, boils at 142—143° under 50 mm. and at 236—238° under 760 mm. pressure and has a sp. gr. 0·7814 and n_D 1·4360 at 20°; its *chloro*-derivative, $C_{14}H_{29}Cl$, boils at 150—153° under 20 mm. pressure, and has a sp. gr. 0·9185; the *dichloro*-derivative, $C_{14}H_{28}Cl_2$, boils at 175—180° under 12 mm. pressure and has a sp. gr. 1·032 at 20°.

Pentadecane, $C_{15}H_{32}$, boils at 158—159° under 50 mm. and at 256—257° under 760 mm. pressure and has a sp. gr. 0·7896 and n_D 1·4413 at 20°; the *dichloro*-derivative, $C_{15}H_{30}Cl_2$, boils at 175—180° under 13 mm. pressure and has a sp. gr. 1·0045 at 20°.

Hexadecane, $C_{16}H_{34}$, boils at 174—175° under 50 mm. and at 275—276° under 760 mm. pressure and has a sp. gr. 0·7911 and n_D 1·4413 at 20°; the *dichloro*-derivative, $C_{16}H_{32}Cl_2$, boils at 205—210° under 16 mm. pressure and has a sp. gr. 1·0314 at 20°.

Heptadecane, $C_{17}H_{36}$, boils at 188—190° under 50 mm. and at 288—289° under 760 mm. pressure and has a sp. gr. 0·8000 at 20°; the *chloro*-derivative, $C_{17}H_{35}Cl$, boils at 175—177° under 15 mm. pressure and has a sp. gr. 0·8962 at 20°.

The fraction which boiled at 199—200° under 50 mm. and at 300—301° under 760 mm. pressure had a sp. gr. 0·8017 at 20° and furnished a *chloro*-derivative, $C_{18}H_{37}Cl$, which boiled at 185—190° under 15 mm. pressure and had a sp. gr. 0·9041 at 20°. When this fraction was cooled to −10°, a white, solid octodecane, $C_{18}H_{38}$, separated, which melts at 20° and has a sp. gr. 0·7830 at 20°/20° and 0·7816 at 40°/20°, and n_D 1·440. After the solid hydrocarbon had been removed by filtration, the liquid portion had a sp. gr. 0·8110 at 20°, n_D 1·4435, and a composition indicating that it was a mixture of the two hydrocarbons, $C_{18}H_{38}$ and $C_{18}H_{36}$.

The fraction boiling at 210—212° under 50 mm. pressure had a sp. gr. 0·8122 and n_D 1·4522 at 20°. On cooling this fraction to −10°, solid nonodecane, $C_{19}H_{40}$, separated, which melts at 33—34° and has a sp. gr. 0·7725 at 30°/30° and 0·7781 at 40°/30°; the filtered oil had the composition $C_{19}H_{38}$, a sp. gr. 0·8208, and n_D 1·4515 at 20°.

The distillate collected at 230—232° under 50 mm. pressure had a sp. gr. 0·8230 and n_D 1·4608 at 20°; it consisted of a solid heneicosane,

$C_{21}H_{44}$, melting at 40—41°, and a liquid hydrocarbon, $C_{21}H_{42}$, which has a sp. gr. 0·8424 at 20°.

The fraction boiling at 240—242° under 50 mm. pressure had a sp. gr. 0·8230 and n_D 1·454 at 20°. On cooling, it deposited a solid docosane, $C_{22}H_{46}$, which melts at 44° and has a sp. gr. 0·7796 at 60°; the liquid portion, $C_{22}H_{44}$, had a sp. gr. 0·8296 at 20°.

The portion collected at 258—260° under 50 mm. pressure had a sp. gr. 0·8341 at 60°, 0·8320 at 70°, and 0·8310 at 80°. It furnished a small proportion of a solid tricosane, $C_{23}H_{48}$, which melts at 45° and has a sp. gr. 0·7894—0·7900 at 60°; the filtered liquid, $C_{23}H_{46}$, had a sp. gr. 0·8569 and n_D 1·4714 at 20°.

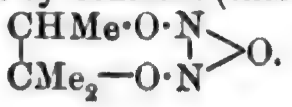
The distillate, at 272—274° under 50 mm. pressure, consisted of a solid tetracosane, $C_{24}H_{50}$, which melts at 48° and has a sp. gr. 0·7902 at 60°, 0·7893 at 70°, and 0·7875 at 80°, and a liquid hydrocarbon, $C_{24}H_{48}$, which has a sp. gr. 0·8582 at 40°/20° and n_D 1·4726.

The fraction boiling at 280—282° under 50 mm. pressure yielded a solid pentacosane, $C_{25}H_{52}$, which crystallises in plates and melts at 53—54°; the liquid portion, $C_{26}H_{52}$, had a sp. gr. 0·8580 and n_D 1·4725.

The portion collected at 292—294° under 50 mm. pressure was composed of a solid hexacosane, $C_{26}H_{54}$, melting at 58°, and a thick, viscous oil, $C_{27}H_{52}$, which had a sp. gr. 0·8688 at 26° and n_D 1·4722.

The distillate, at 310—312° under 50 mm. pressure, furnished a solid octocosane, $C_{28}H_{58}$, which melted at 60° and had a sp. gr. 0·7945 at 70°, 0·7927 at 80°, and 0·7911 at 90°, and a thick oil, $C_{28}H_{54}$, which had a sp. gr. 0·8694 and n_D 1·480. E. G.

Desmotropism of Trimethylethylene Nitrosite. By Arthur Hantzsch (*Ber.*, 1902, **35**, 2978—2980).—A discussion of the constitution of the additive product of nitrogen trioxide and β-methyl-Δ^{β}-butylene described by Schmidt (this vol., i, 581), for which the author prefers the formula



$$\left.\begin{array}{l}\text{CHMe}\cdot\text{O}\cdot\text{N}\\ \text{CMe}_2\text{—O}\cdot\text{N}\end{array}\right>\text{O}.$$

R. H. P.

Connection between Bisnitrosyl Compounds and Nitroso-compounds. By Oscar Piloty (*Ber.*, 1902, **35**, 3090—3093).—Comparing the properties of the nitroso-compounds described in the two following papers, the author concludes that there is no essential difference between nitroso-compounds and the bisnitrosyl compounds which contain the N_2O_2 group. On the contrary, the transition from the one class to the other is gradual; the typical nitroso-compounds are unimolecular liquids or crystallised solids of a deep blue colour; some nitroso-compounds form colourless solids which become blue when melted or dissolved, and these are bimolecular in the cold and contain the N_2O_2 group. The difficulty of resolving the N_2O_2 group into two NO groups increases until finally the typical bisnitrosyl compounds are arrived at, and these no longer show the blue colour under any conditions. J. McC.

Constitution of ψ-Nitroles and some Bromonitrosohydrocarbons. By Oscar Piloty and A. Stock (*Ber.*, 1902, **35**, 3093—3101).—*Propyl-ψ-nitrole*, prepared from β-bromo-β-nitrosopropane by shaking in ethereal solution with silver nitrite, forms white crystals which melt at 76°.

β-Bromo-β-nitrosobutane, formed when methylethylketoxime in aqueous solution is treated with bromine in presence of pyridine, is a deep blue, volatile liquid which boils at 28° under 19 mm. pressure and has a sp. gr. 1·360 at 22°. With silver nitrite, it gives *butyl-ψ-nitrole*, which melts at 58°.

In the same way, from diethylketoxime, *β-bromo-β-nitrosopentane* is formed as a liquid which boils at 49° under 17 mm. pressure and has a sp. gr. 1·325 at 20°; with silver nitrite, it gives amyl-ψ-nitrole melting at 63·5°.

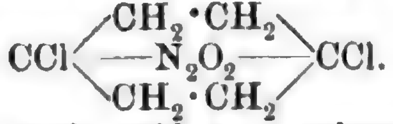
By the action of bromine in presence of pyridine on the oxime obtained by treating pinacolin with hydroxylamine, *γ-bromo-γ-nitroso-ββ-dimethylbutane* is produced. It forms volatile, blue crystals with an odour recalling that of camphor.

The formation of bromonitroso-compounds is a useful test for ketones. The solution to be tested should be made neutral, and to it a drop of a 10 per cent. solution of hydroxylamine hydrochloride and one of a 5 per cent. solution of sodium hydroxide added. A large drop of pyridine is introduced and a thin layer of ether poured on, after which it is shaken with sufficient bromine to impart a yellow colour to the ether. If, on addition of hydrogen peroxide, the ether becomes blue, the presence of a ketone or ketonic group may be concluded.

When butyl-ψ-nitrole is dissolved in anhydrous hydrogen cyanide at −10°, the solution is colourless; the depression of the freezing point of the hydrogen cyanide was observed, and again, after standing, when the solution had become quite blue. It was found that the second depression was exactly double the first, indicating that in the colourless form the ψ-nitrole has a doubled molecular formula.

From the transformation of the bromonitroso-compounds into ψ-nitroles with silver nitrite, the authors conclude that the former are true nitroso-compounds. J. McC.

Halogenated Nitroso-compounds of Diketo*cyclo*hexamethylene and a Secondary Nitroso-compound. By Oscar Piloty and Hermann Steinbock (*Ber.*, 1902, 35, 3101—3117).—By the action of bromine, in presence of pyridine, on the dioxime of *p*-diketo*cyclo*hexane, 1 : 4-*dibromo*-1 : 4-*dinitroso*cyclo*hexane* is formed; it crystallises in deep blue, rhombic pyramids, melts at 89°, and is very easily soluble in alcohol, acetic acid, ether, or benzene. In this reaction, it is the *cis-trans*-modification which is formed, and there is also produced 1 : 4-*dibromo*-1 : 4-*bisnitrosyl*cyclo*hexane* which is colourless and insoluble in ether. Nitric acid or chromic and acetic acids transform the nitroso-compound into 1 : 4-*dibromo*-1 : 4-*dinitro*cyclo*hexane*, which melts at 158° and is insoluble in water, but easily soluble in alcohol, ether, or acetic acid.

When a current of chlorine is passed through a cooled hydrochloric acid solution of *p*-diketo*cyclo*hexanedioxime, the *cis-trans*-modification of 1 : 4-*dichloro*-1 : 4-*dinitroso*cyclo*hexane* is produced. It is formed much more easily than the corresponding bromo-compound and does not require the presence of pyridine. It forms deep blue, monoclinic prisms, melts at 108·5°, and is easily soluble in the common organic solvents. When hydrogen chloride is passed through a solution of it in glacial acetic acid, it changes into 1 : 4-*dichloro*-1 : 4-*bisnitrosyl*cyclo*hexane*, which separates in colourless crystals. This represents a new class of intermolecular bisnitrosyl compounds for which the formula developed is  $CCl\left\langle\begin{array}{c}CH_2\cdot CH_2\\ -N_2O_2-\\ CH_2\cdot CH_2\end{array}\right\rangle CCl$. It is soluble in methyl alcohol, acetone, or acetic acid to a colourless solution which, when heated, becomes blue, and again colourless when cooled. This characteristic reaction is attributed to its conversion into a nitroso-compound at the higher temperature. With chromic and acetic acids, the chloronitroso-compound gives 1 : 4-*dichloro*-1 : 4-*dinitro*cyclo*hexane* as a greenish substance which melts at 178° and is soluble in the ordinary organic solvents.

By the action of chlorine on benzaldoxime, a very unstable, blue substance is formed which the authors believe to be *ω-chloro-ω-nitrosotoluene*, CHPhCl·NO.

With acetaldoxime in hydrochloric acid solution, chlorine gives *monochloronitrosoethane*, which can be obtained in colourless plates; it dissolves in ether or methyl alcohol with a deep blue colour and melts at 65° to a blue liquid which becomes colourless on solidifying. It is spontaneously transformed into acetohydroximic acid chloride ($CHMeCl\cdot NO \rightarrow CMeCl\colon N\cdot OH$), which solidifies at −3°. When dissolved in hydrochloric acid and treated with chlorine, this hydroximic acid chloride gives *dichloronitrosoethane*, $CH_3\cdot CCl_2\cdot NO$, as a liquid which boils at 68°(corr.); it is miscible with alcohol, ether, or benzene, but not with water, and has a sp. gr. 1·2521 at 19°.

The constant for the molecular depression of the freezing point of anhydrous hydrogen cyanide has been determined to be 21·7, and a normal molecular weight has been found for dichloronitrosoethane in this solvent. J. McC.

Formation of Alcohols by the Electrolysis of the Salts of the Fatty Acids. By Hans Hofer and M. Moest (*Annalen*, 1902, **323**, 284—323).—Methyl alcohol is produced when sodium acetate is electrolysed in aqueous solutions containing sodium perchlorate; under similar conditions, the corresponding propionate and *n*- and *iso*-butyrates give rise to ethyl and *n*- and *iso*-propyl alcohols respectively. Sodium succinate yields hydracrylic acid instead of ethylene glycol. Other inorganic salts induce this reaction, namely, chlorates, sulphates, carbonates, and hydrogen carbonates. The aldehydes corresponding with the alcohols are also formed during the electrolysis. Only small quantities of the alcohols and aldehydes are obtained on electrolysing valerates and hexoates.

The communication includes a detailed account of the apparatus employed and tables indicating the composition of the gases produced with solutions of varying concentration (compare Abstr., 1894, i, 228; 1896, i, 10, 664). G. T. M.

Action of Alcohols on Esters. By Louis Henry (*Bull. Acad. Roy. Belg.*, 1902, 445—494).—The action of alcohols on esters is not dependent simply on the reactive intensity of the alcohol (measured by its esterification velocity for acetic acid) except in the cases of the action of methyl or ethyl alcohol on amyl, glyceryl, and cellulose nitrites (compare Bertoni, Abstr., 1886, 217, and 1887, 458) and of the same alcohols on mixed acid anhydrides (compare Behal, Abstr., 1899, i, 734), which the author regards as a class of esters.

In many cases, the action is modified by the reactive intensity of the acid residue of the ester, thus, pyruvyl formate, $CH_2Ac\cdot O\cdot CHO$, is decomposed by methyl alcohol with the liberation of pyruvyl alcohol (a small amount of the corresponding ether melting at 130° is also formed), whilst pyruvyl acetate is not attacked.

Temperature is also an important factor, thus, whilst amyl nitrite is decomposed in the cold by methyl or ethyl alcohol, it is not attacked by propyl or butyl alcohol until heated, although these possess higher reactive intensities than amyl alcohol. In some cases, the effect of temperature is to invert the action altogether, thus: glycol, when boiled with diethyl succinate, liberates ethyl alcohol, although the reactive intensities of the two alcohols are respectively 66·5 and 53·9, the abnormality being due to the greater volatility of ethyl alcohol (compare Vorländer, Abstr., 1895, i, 17).

It is probable also that solubility plays a considerable part in influencing actions of this type.

Functional inertia of the alcohol may also be overcome by greatly increasing its reacting mass, relatively to that of the ester (compare Walker, Abstr., 1893, i, 500, and Vorländer, *loc. cit.*).

Reactive intensity in a homologous series of alcohols decreases as the series is ascended, and the same result is produced by the introduction of negative groups such as OH, Cl, CO, the effects of these increasing with their proximity to the original OH group of the alcohol (compare Heintz, *Annalen*, 1861, 114, 440; Bertoni, *loc. cit.*; Richter, this Journal, 1877, ii, 439; Rose, Abstr., 1881, 251; Bachmann, Abstr., 1883, 726; Behal, *loc. cit.*; Henry, Abstr., 1901, i, 577; Vorländer, *loc. cit.*), where reactions illustrating this general statement are to be found. In the original paper, explanations of these reactions embodying the foregoing views are given. T. A. H.

Mono-ethers of Bivalent Alcohols. By M. H. Palomaa (*Ber.*, 1902, **35**, 3299—3301).—By treating ethylene glycol with sodium and an alkyl iodide, the mono-ethers are obtained. *Glycol monomethyl ether*, $OMe\cdot CH_2\cdot CH_2\cdot OH$, boils at 124—125°, has an ethereal odour and a sp. gr. 0·9703 at 19°/19°, and is miscible with water. With acetic anhydride, it gives an *acetate* of the formula $OMe\cdot CH_2\cdot CH_2\cdot OAc$, which boils at 144·5—145° and has a sp. gr. 1·0090 at 19°/19°.

The *mono-*n*-propyl ether* of *ethylene glycol*, $Pr\cdot O\cdot CH_2\cdot CH_2\cdot OH$, boils at 152—153° and has a sweet odour and a sp. gr. 0·9159 at 19°/19°.

J. McC.

Products which are Formed by simultaneously passing Dry Sulphur Dioxide and Ammonia into Absolute Alcohol distilled over Sodium. By Alwin Goldberg and M. R. Zimmermann (*Zeit. angew. Chem.*, 1902, **15**, 898—906).—The ammonium sulphites, obtained by passing sulphur dioxide and ammonia into absolute alcohol, were first prepared by Muspratt (*Annalen*, 1844, **50**, 269), and subsequently studied in detail by Schumann (Abstr., 1900, ii, 271). Divers (Trans., 1899, **75**, 533) prepared ammonium ethyl sulphite by using carefully dried alcohol and a low temperature, − 15°. The authors have prepared the same compound, which they call *ammonium ethoxysulphinate*, at the ordinary temperature; it is decomposed by hot water into ammonium pyrosulphite and alcohol. *Ammonium methoxysulphinate*, $OMe\cdot SO\cdot ONH_4$, is prepared similarly, as are also the analogous derivatives of amyl alcohol, methylethylcarbinol, and trimethylcarbinol. The *compound* from allyl alcohol is formed by union of 3 mols. of ammonia and sulphur dioxide respectively, and 2 mols. of allyl alcohol; from the fact that only two-thirds of the sulphur dioxide can be titrated by iodine, the salt is represented by the formula $ONH_4\cdot SO\cdot O\cdot[CH_2]_3\cdot SO_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot O\cdot SO\cdot ONH_4$.

On leading ammonia into molten ammonium ethyl sulphite at 99°, *ammonium aminosulphinate*, $NH_2\cdot SO\cdot ONH_4$, is formed. When ammonium ethyl sulphite is heated, ammonium sulphate is formed; when heated under pressure with absolute alcohol or ethyl bromide, ammonium sulphate and thiosulphate are produced; if the salt is heated alone under pressure, besides ammonium sulphate and sulphur, a yellow oil, $C_4H_{10}O_4S_3$, which is volatile with steam, is obtained. Ammonium methyl sulphite decomposes in a similar manner. K. J. P. O.

Action of Acid Chlorides and Anhydrides of the Fatty Series on Trioxymethylene. By Marcel Descudé (*Bull. Soc. Chim.*, 1902, [iii], **27**, 867—871. Compare Abstr., 1901, i, 644, and this vol., i, 149, 339, 451).

—When trioxymethylene reacts with acetyl chloride in presence of zinc chloride, there are formed chloromethyl acetate, dichloromethyl oxide, and methylene diacetate; the last, which boils at 170°, is also formed by the action of acetic anhydride on trioxymethylene in presence of zinc chloride. In this reaction, there is also produced *methyleneoxide diacetate*, $(Me\cdot CO_2\cdot CH_2)_2O$, which distils at a temperature of 204—207°. In a similar manner, there have been prepared *chloromethyl propionate*, boiling at 128—130°, sp. gr. 1·140; *methylene dipropionate*, boiling at 190—192°, sp. gr. 1·503; *chloromethyl isobutyrate*, boiling at 138—140°, sp. gr. 1·080; *methylene diisobutyrate*, boiling at 197—199°, sp. gr. 0·998; *chloromethyl butyrate*, boiling at 150°, sp. gr. 1·094; *methylene dibutyrate*, boiling at 215—216°, sp. gr. 1·017; in all cases, the boiling points were determined under a pressure of 745 mm. and the sp. gr. taken at 20°/20°.

Some of the commercial specimens of trioxymethylene are not suitable for the above reactions, but a suitable specimen can be obtained by slowly evaporating a solution of formaldehyde. A. F.

Wood Tar of the Douglas Fir (Pseudotsuga Taxifolia). By H. G. Byers and Paul Hopkins (*J. Amer. Chem. Soc.*, 1902, **24**, 764—771).

—When the wood was distilled at temperatures below 400°, there were obtained (A) 47·5 per cent. pyroligneous acid, containing acetic acid 3·47 per cent., and methyl alcohol 4·16 per cent.; (B) 7·5 per cent. of tar containing light oil 18·0, creosote oil 23·0, pitch 39·0, and water 20·0 per cent.; (C) 30·0 per cent. of charcoal;

and (D) 15·0 per cent. of gas. At temperatures below 700°, there were obtained (A) pyroligneous acid 34 per cent., containing acetic acid 2·9, and methyl alcohol 2·9 per cent.; (B) tar 17·7 per cent., containing light oil 8·0, creosote oil 10·0, pitch 18·0, and water 64·0 per cent.; (C) charcoal 29 per cent., and (D) gases 19·3 per cent.

The gas is non-illuminating; the charcoal is soft and contains little ash.

The creosote oil boiled from 150—250° and contained 17 per cent. of creosote, of which 9·5 per cent. was guaiacol.

The light oil, which boiled between 40° and 150°, was fractionated, and contained small amounts of aldehydes and ketones and considerable amounts of the methyl and ethyl esters of formic, acetic, propionic, and butyric acids. The results of the fractionation and the yield of the products are tabulated in the original. T. A. H.

Behaviour of Certain Acyl Chlorides towards Agents which eliminate Hydrogen Chloride. By EDGAR WEDEKIND (*Annalen*, 1902, **323**, 246—257).—Acetyl chloride, when treated with triethylamine dissolved in benzene, loses hydrogen chloride and 4 mols. of the residue condense to form dehydracetic acid; its next homologue, propionyl chloride, behaves differently under these conditions, giving rise to a trimeric condensation product. Compounds of similar complexity have also been obtained from phenylacetyl chloride and dihydrocinnamyl chloride.

Dehydracetic acid also results from the action of ferric chloride on acetyl chloride. The homologous chlorides of the fatty series, when condensed with dry metallic chlorides, yield high-boiling oils, the constitution of which is not yet known. Benzoyl chloride and phenylacetyl chloride do not give rise to ketones under the influence of ferric chloride. The aromatic acyl chlorides containing at least three carbon atoms in the side chain condense to form cyclic ketones; dihydrocinnamyl chloride yields hydrindone, whilst phenyl-*n*-butyryl chloride and phenyl-*n*-valeryl chloride furnish *a*-ketotetrahydronaphthalene and pheno-*a*-keto*cyclo*heptane respectively. Cinnamyl chloride does not, however, condense to form an indenone.

Aluminium chloride also serves to promote these condensations. In ethereal solutions, the acyl chlorides, under the influence of the anhydrous metallic chlorides, give rise to the ethyl esters of the corresponding acids. G. T. M.

Nature of Radicles. By EDGAR WEDEKIND (*Annalen*, 1902, **323**, 257—264. Compare Vorländer, this vol., i, 309; ii, 250).—Ethyl chlorocarbonate does not form additive products with the strong tertiary bases, although it is readily decomposed by these substances, the action being accompanied by an elimination of hydrogen chloride. It follows therefore that this acyl chloride conforms to the author's rule that two negative groups, one of which is a strongly acidic radicle, do not, under ordinary conditions, form additive products with the tertiary amines. The author's study of the interaction of acyl chlorides and the tertiary bases leads to the following conclusions. The more rapid and complete is the interaction of these reagents, the greater is the probability of an elimination of hydrogen from the molecule of the acyl chloride and the consequent formation of bye-products. On the other hand, the slower the elimination of hydrogen chloride, the greater is the tendency for the intervention of moisture, leading to the production of acid anhydrides.

Pyridine picryl chloride, $C_5NH_5Cl{\cdot}C_6H_2(NO_2)_3$, results from the addition of picryl chloride to pyridine; it is a yellow, amorphous powder, readily decomposed by water or the hydroxylic solvents with the production of pyridine picrate. Triethylamine appears to yield a similar product, but no addition takes place in the case of tripropylamine. G. T. M.

Linseed Oil. By S. Fokin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 501—503).—Contrary to the observations of some other investigators, the chief constituent of linseed oil is found to be linolic acid, together with 22—25 per cent. of linolenic acid and about 5 per cent. of solid fatty acids.

The linolic acid contained in linseed oil is apparently isomeric with those obtained from cotton-seed oil and sunflower oil. The tetrabromostearic acid prepared from linseed oil is difficult to obtain in a solid state, and then forms an amorphous mass melting at 98—101°, whilst the similar acid from other oils is distinctly crystalline and melts at 114—115°. T. H. P.

Action of Organic Acids on Antimony Oxides. By Eduard Jordis (*Zeit. angew. Chem.*, 1902, **15**, 906—911).—The power possessed by organic acids of dissolving antimonious oxide depends entirely on the relative strength of the acids. The recent publications of Moritz and Schneider (this vol., i, 703) are criticised. K. J. P. O.

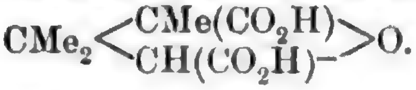
Electrolytic Study of Pyruvic Acid. By George W. Rockwell (*J. Amer. Chem. Soc.*, 1902, **24**, 719—734).—When pyruvic acid, dissolved in alcohol, is oxidised electrolytically, in presence of sodium hydroxide or carbonate, or of sulphuric or hydrochloric acid, used as electrolytes, there are formed in quantities varying with the concentration, temperature, current strength, and voltage employed, acetaldehyde, ethyl acetate, carbon monoxide and dioxide, but no acetyl peroxide. When the acid is electrolytically reduced, using the same electrolytes, the amount of lactic acid produced is similarly dependent on the same factors. T. A. H.

Condensation of Carbon Tetrachloride with Ethyl Malonate and Ethyl Cyanoacetate. By Otto Dimroth (*Ber.*, 1902, **35**, 2881—2884).—In the hope of synthesising allene derivatives (·C:C:C·), carbon tetrachloride and ethyl disodiocyanoacetate were caused to interact; the sodium salt of ethyl dicyanoglutaconate (Errera, Abstr., 1898, i, 297; and Ruhemann and Browning, Trans., 1897, **73**, 280) was obtained and identified by conversion into the ester (m. p. 181—183°); on boiling with alcohol, the latter yielded the
ace nium salt of ethyl 2 : 6-dihydroxypyridine-3 : 5-dicarboxylate
7·5 pe 9°). On reinvestigation of the allene derivative, ethyl allene-
pitch 39·

tetracarboxylate, which was prepared by Zelinsky and Doroschewsky (Abstr., 1895, i, 129) by the action of ethyl disodiomalonate on carbon tetrachloride, it was found that this substance was ethyl ethoxycoumalindicarboxylate (m. p. 94°), originally prepared by Guthzeit and Dressel (Abstr., 1889, 860) by the action of heat on ethyl dicarboxyglutaconate. Further, the first product of the action of carbon tetrachloride and ethyl disodiomalonate is not ethyl ethoxypropylenetetracarboxylate, as Zelinsky and Doroschewsky believed, but ethyl dicarboxyglutaconate (Conrad and Guthzeit, Abstr., 1884, 297).

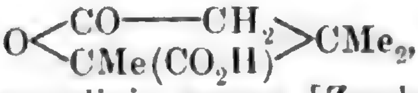
Carbon tetrachloride and the disodio-derivatives of ethyl cyanoacetate and ethyl malonate yield the same products as chloroform and the monosodio-derivatives of these esters. K. J. P. O.

Isomeric Lactonic Acids Derived from $\beta\gamma\gamma$-Dimethyl-β-hydroxypentanedioic Acid. By Luigi Balbiano (*Gazzetta*, 1902, **32**, i, 485—494).—The acid described by the author (Abstr., 1899, i, 867) as $\gamma\gamma\delta$-trimethylpentane-$\beta\epsilon$-olidoic acid is now found to be a mixture of two isomerides, one $\gamma\gamma\delta$-trimethylpentane-$\beta\epsilon$-olidoic acid, and the other $\beta\gamma\gamma$-trimethylpentane-$\beta\epsilon$-olidoic acid, identical with the acid obtained by Blanc (Abstr., 1901, i, 119). It follows from this that the acid, $C_8H_{12}O_5$, obtained as the chief oxidation product of camphoric acid, does not possess the constitution $CO_2H\cdot CO\cdot CMe_2\cdot CHMe\cdot CO_2H$, assigned to it by Tiemann and Mahla (Abstr., 1895, i, 678), since such an acid should give on reduction exclusively $\gamma\gamma\delta$-trimethylpentane-$\beta\epsilon$-olidoic acid; as, however, this acid, $C_8H_{12}O_5$, when reduced gives a mixture of the two isomerides mentioned above, it must have the formula



$$CMe_2<\begin{matrix}CMe(CO_2H)\\CH(CO_2H)-\end{matrix}>O.$$

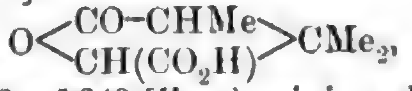
$\beta\gamma\gamma$-Trimethylpentane-$\beta\epsilon$-olidoic acid,



$$O<\begin{matrix}CO\text{——}CH_2\\CMe(CO_2H)\end{matrix}>CMe_2,$$

melts at 165—166° and crystallises in the monoclinic system [Zambonini, $a:b:c=0{\cdot}54867:1:1{\cdot}0863.\quad \beta=52°5'30''$].

$\gamma\gamma\delta$-Trimethylpentane-$\beta\epsilon$-olidoic acid,

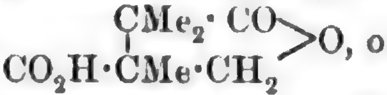


$$O<\begin{matrix}CO-CHMe\\CH(CO_2H)\end{matrix}>CMe_2,$$

also forms monoclinic crystals melting at 163—164° [Zambonini, $a:b:c=0{\cdot}47994:1:1{\cdot}2802.\quad \beta=83°38'$]. The *calcium* salt crystallises with $4H_2O$; the *lead* salt ($+3H_2O$) separates from water in mammillary tufts of small needles melting at 110—112°, whilst in the anhydrous form it softens at 176° and melts at 184—185°.

The mixture of the two acids does not melt at 110—120° as Blanc (*loc. cit.*) stated, but at 158—160°. T. H. P.

Camphoric Acid. XII. Synthesis of Trimethylparaconic Acid. By William A. Noyes and Austin M. Patterson (*Amer. Chem. J.*, 1902, **28**, 228—232; *Ber.*, 1902, **35**, 2940—2942).—*Trimethylparaconic acid,*



$$\begin{matrix}CMe_2\cdot CO\\ |\\ CO_2H\cdot CMe\cdot CH_2\end{matrix}>O,$$

obtained by heating a mixture of sodium trimethylsuccinate, trioxymethylene, and acetic anhydride in a sealed tube at 120—140° for two days, crystallises from hot benzene or dilute alcohol and melts and decomposes at 256—257°; its *ethyl* ester melts at 34·5°. When the acid is warmed with sodium hydroxide, it is converted into *sodium trimethylitamalate*,

$$CO_2Na \cdot CMe_2 \cdot CMe(CH_2 \cdot OH) \cdot CO_2Na;$$

the corresponding *silver* salt was prepared and analysed. *Diethyl trimethylitamalate* was obtained as a viscous oil; when treated with phosphorus tribromide, it is converted into ethyl trimethylparaconate

E. G.

Anæropolarimetry. By B. H. J. TER BRAAKE (*Rec. trav. chim.*, 1902, **21**, 155—185).—The author has investigated the optical rotation of ethyl monosodium and monopotassium tartrates and of disodium and dipotassium tartrates in alcoholic solution, special precautions having been taken to avoid the absorption of water from the air. The substances are all lævorotatory, a fact which is contrary to Guye's hypothesis. The rotation of the last two compounds could not be determined exactly. The rotatory power of the monosubstituted esters increases as the concentration is increased and as the temperature is lowered. The rotatory power of the above compounds also undergoes change with time, owing to the formation of ethyl mono- and di-sodium and potassium mesotartrates and of ethyl mono- and di-sodium and potassium racemates; in the case of ethyl monosodium tartrate, the major portion is transformed into the mesotartrate.

A. F.

Action of Water on the Ethyl Monosodium and Monopotassium Tartrates. By B. H. J. TER BRAAKE (*Rec. trav. chim.*, 1902, **21**, 186—190. Compare Mulder, Abstr., 1890, 595).—By the action of water on the ethyl monosodium and monopotassium tartrates, a gelatinous precipitate separates, consisting of a mixture of ethyl sodium or potassium tartrate and of disodium or dipotassium tartrate.

A. F.

Action of Halogen-substituted Esters of Fatty Acids on the Sodio-compounds of Saturated and Unsaturated Derivatives of Ethyl Malonate. By MAX GUTHZEIT and MAX ENGELMANN (*J. pr. Chem.*, 1902, [ii], **66**, 104—129. Compare this vol., i, 658).—*Ethyl Δ^{a}-butylene-aγγδ-tetracarboxylate*,

$$CO_2Et \cdot CH \colon CH \cdot C(CO_2Et)_2 \cdot CH_2 \cdot CO_2Et,$$

prepared by the action of ethyl bromoacetate and sodium ethoxide on ethyl *iso*aconitate, is an oil which boils at 216—218° under 14 mm. pressure, and when hydrolysed by 50 per cent. hydrochloric acid yields *Δ^{a}-butylene-aγδ-tricarboxylic acid*, which melts at 148°, is easily soluble in water or acetone, but sparingly so in ether, benzene, or chloroform, and gives precipitates in neutral solution with silver, lead, and copper salts. *Ethyl butane-aββδ-tetracarboxylate*, obtained by the action of ethyl bromoacetate and sodium ethoxide on ethyl carboxyglutarate (b. p. 161° under 12 mm. pressure; compare Abstr., 1899, i, 261), is a colourless liquid, which boils at 200—205° under 15 mm. pressure, and when hydrolysed by 10 per cent. hydrochloric acid yields aβδ-butanetricarboxylic acid, which melts at 118—120° (compare Abstr., 1892, 42), is easily soluble in acetone, but sparingly so in ether or chloroform, and, when neutralised with ammonia, gives precipitates with copper, iron, silver, and lead salts.

The action of ethyl chloromalonate on ethyl sodiodicarboxyglutaconate leads to the formation of an oil, probably *ethyl* Δ^{α}-*butylene-ααγγδδ-hexacarboxylate*, which commences to decompose at 230° under 15 mm. pressure, and, on hydrolysis with dilute hydrochloric acid, yields Δ^{α}-butylene-αγδ-tricarboxylic acid.

Ethyl bromoacetate reacts more easily than ethyl chloroacetate with ethyl sodiodicarboxyglutaconate, giving a better yield of ethyl butylenepentacarboxylate (this vol., i, 659), which is hydrolysed by dilute hydrochloric acid to butylenetricarboxylic acid. Ethyl butanepentacarboxylate, formed by reduction of the unsaturated ester with zinc dust in glacial acetic acid solution, boils at 218—220° under 12 mm. pressure.

The action of ethyl bromoacetate on ethyl sodiobutanepentacarboxylate in absolute alcohol leads to the formation of *ethyl pentane-αββδδε-hexacarboxylate*, which crystallises from light petroleum in nacreous leaflets, melts at 62°, boils at 230—240° under 12 mm. pressure, is easily soluble in ether, chloroform, or benzene, but more sparingly so in alcohol or light petroleum, and on hydrolysis with 15 per cent. hydrochloric acid yields *pentane-αβδε-tetracarboxylic acid* (*methylenedisuccinic acid*), $CH_2[CH(CO_2H)\cdot CH_2\cdot CO_2H]_2$, which forms crystalline nodules, melts and effervesces at 214—216°, is sparingly soluble in cold water or acetone, and almost insoluble in ether, benzene, or chloroform. The zinc and barium salts are precipitated only in boiling solutions and redissolve on cooling.

Ethyl pentane-αββδδε-hexacarboxylate can also be obtained in a 20 per cent. yield by the action of ethyl bromoacetate on ethyl disodiodicarboxyglutarate. There is formed in the same reaction an oil which boils at 195—200° under 12 mm. pressure, and must be ethyl propane-αββγ-tetracarboxylate, $CO_2Et\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CO_2Et$ (Bischoff, Abstr., 1883, 46), or ethyl propane-ααβγ-tetracarboxylate, $CO_2Et\cdot CH_2\cdot CH(CO_2Et)\cdot CH(CO_2Et)_2$ (Emery, Abstr., 1891, 424), as on hydrolysis it yields tricarballylic acid.

The action of methyl chloromalonate on methyl disodiodicarboxyglutarate leads to the formation of methyl trimethylenetetracarboxylate (m. p. 73°) and methyl ethanetetracarboxylate (m. p. 137—138°).

Methyl heptane-αγγεεη-hexacarboxylate,

$$CH_2[C(CO_2Me)_2\cdot CH_2\cdot CH_2\cdot CO_2Me]_2,$$

formed by the action of methyl β-iodopropionate on methyl disodiodicarboxyglutarate, melts at 87° and boils at 170—190° under 14 mm. pressure.

Ethyl dicarboxyglutarate is more easily obtained in a pure state by the action of methylene iodide on ethyl sodiomalonate than by the action of formaldehyde on ethyl malonate in the presence of diethylamine. Ethyl pentane-ααγεε-hexacarboxylate (compare Bottomley and Perkin, Trans., 1900, **77**, 294), which is formed in the later reaction, yields, with ammonia, a *hexa-amide*, $C(CO\cdot NH_2)_2[CH_2\cdot CH(CO\cdot NH_2)_2]_2$, which sinters above 210°, melts at 230—235°, and on hydrolysis with hydrochloric acid forms pentane-αγε-tricarboxylic acid. G. Y.

Cystein. I. By CARL NEUBERG (*Ber.*, 1902, **35**, 3161—3164. Compare Baumann, Abstr., 1882, 1).—*iso*Ethionic acid is produced when cystein is oxidised with nitric acid of sp. gr. 1·2. This would indicate that the sulphydryl and amino-groups are attached to different carbon atoms in the cystein molecule, which, therefore, should have the constitution $CO_2H·CH(SH)·CH_2·NH_2$ or $CO_2H·CH(NH_2)·CH_2·SH$.

J. J. S.

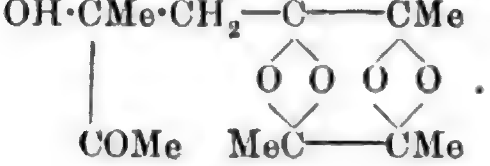
A New Method of preparing Trithioformaldehyde. By LUDWIG VANINO (*Ber.*, 1902, **35**, 3251—3252).—When an acid is added to a solution of sodium thiosulphate containing formaldehyde, no precipitation of sulphur takes place in the cold. On warming the mixture, some sulphur is separated, and ultimately trithioformaldehyde is precipitated.

J. McC.

Preparation of Diacetyl and a Polymerisation Product of Diacetyl. By OTTO DIELS and HANS JOST (*Ber.*, 1902, **35**, 3290—3299).—Diacetyl can be conveniently prepared from methyl ethyl ketone by treatment with amyl nitrite and boiling the *iso*nitrosoketone formed with an acid. Diacetyl, when shaken with concentrated hydrochloric acid, is converted into *termolecular diacetyl*, $C_{12}H_{18}O_6$, which melts at 105°, boils at 280°, and is sparingly soluble in water, but easily so in organic solvents. This polymeric diacetyl does not reduce Fehling's solution, permanganate, or silver solution. It is quite stable in presence of alkalis, but mineral acids decompose it into diacetyl, acetic acid, and other substances not yet identified. With acetic anhydride, it gives a *monoacetyl* derivative which melts at 93°. It forms a *phenylurethane* which crystallises from benzene with one mol. of benzene of crystallisation, melts at 86°, or after freeing from benzene at 132° (corr.). With phenylhydrazine in presence of acetic acid it gives the ordinary osazone of diacetyl. It forms a *p-nitrophenylhydrazone* which melts at 200° (corr.), an *oxime* which melts at 174—175° (corr.), and a *semicarbazone* melting at 238° (corr.). The acetyl derivative gives a *semicarbazone* which melts at 206° (corr.).

When reduced with sodium amalgam, the polymeric diacetyl yields *p*-xyloquinol and a substance which is probably dimethyl*cyclo*hexanone. The latter gives a *semicarbazone* melting at 198° (corr.).

From the behaviour of the polymeric diacetyl, it is evident that it contains a hydroxyl radicle and a ketonic group as well as four indifferent oxygen atoms; the formula provisionally suggested for it is:



J. McC.

Action of Soluble Ferments and Top Yeast on Gentiobiose. By ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1902, **135**, 399—401. Compare this vol., i, 713).—The soluble ferments of *Aspergillus* completely hydrolyse gentiobiose into 2 mols. of dextrose.

Emulsin, which hydrolyses gentiobiose, has only a slight action on gentianose, causing its solution to become more dextrorotatory. Top yeast, on the other hand, partially hydrolyses gentianose, but does not attack gentiobiose.

Sucrose, raffinose, gentianose, and manneotetrose are all partially hydrolysed by invertin with the liberation of 1 mol. of lævulose; gentiobiose, on the contrary, is not affected by this reagent.

In order to hydrolyse gentianose completely by these ferments it is therefore necessary to treat it successively with invertin and emulsin. G. T. M.

Formaldehyde (Methylene) Derivatives of Sugars and Glucosides. By Cornelis A. Lobry de Bruyn and William Alberda van Ekenstein (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, **5**, 175—177. Compare Abstr., 1900, i, 619).—A number of mono- and di-formal derivatives can be obtained when sugars (and glucosides) are fused with trioxymethylene. Diformalxylose melts at 56—57°, has $[\alpha]_D$ (2 per cent. solution in methyl alcohol) $+25\cdot7°$, and sublimes readily. Diformalarabinose is an oily, colourless liquid boiling at 155° under 32 mm. pressure; $[\alpha]_D$ (2 per cent. solution in methyl alcohol) $-16°$. Methylenegalactoside (mono-formal derivative) is an indistinctly crystalline substance melting at 203°; $[\alpha]_D$ (2 per cent. aqueous solution) $+124\cdot8°$. Formalmethylenefructoside melts at 92° and has $[\alpha]_D$ (2 per cent. aqueous solution) $-34\cdot9°$. From *d*-sorbose, a derivative has been obtained melting at 54°, with $[\alpha]_D$ (2 per cent. aqueous solution) $-25°$; from rhamnose, a product melting at 76° and with $[\alpha]_D$ (0·4 per cent. aqueous solution) $-18°$; mannose also yields a crystalline derivative.

Crystalline formal derivatives were obtained from methylmannoside (m. p. 127°; $[\alpha]_D$ $+10\cdot5$), from β-methyl-*d*-glucoside (m. p. 136°, inactive), and from α- and β-methyl-*d*-galactosides. The derivatives obtained from α-methyl-*d*-glucoside and amyl- and ethyl-*d*-glucosides are viscous liquids. J. C. P.

Preparation of Osones from Osazones derived from Sugars. By Emil Fischer and E. Frankland Armstrong (*Ber.*, 1902, **35**, 3141—3144).—Herzfeld (*Ber.*, 1895, **28**, 442) has shown that benzaldehyde may replace hydrochloric acid in the decomposition of phenylhydrazones. A similar method cannot be adopted in the case of the phenylosazones of the monosaccharides, since, in most cases, they are not sufficiently soluble in water. The phenylosazones of disaccharides, however, are completely decomposed when their aqueous solutions are boiled for a short time with benzaldehyde, and good yields of the osones are obtained. The method is also applicable to the osazones of arabinose and xylose, which are soluble in hot water.

Maltosone has been obtained in the form of a syrup which sets to a vitreous, amorphous mass. It reduces Fehling's solution, and reacts with phenylhydrazine yielding maltosazone; with *p*-bromophenylhydrazine it yields p-*bromophenylmaltosazone*, which crystallises in yellow needles melting and decomposing at 198° and only sparingly soluble in the ordinary solvents with the exception of hot alcohol. Yeast enzymes hydrolyse maltosone to glucosone.

Melibiosone in aqueous solution has a low dextrorotation, and is hydrolysed by emulsin. p-*Bromophenylmelibiosazone* crystallises in yellow needles melting at 182°. J. J. S.

Synthesis of New Disaccharides. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1902, **35**, 3144—3153. Compare E. Fischer, Abstr., 1891, 413).—Three new disaccharides have been obtained by the action of tetra-acetylchlorodextrose on the sodium derivative of galactose and by the action of tetra-acetylchlorogalactose on the sodium derivatives of dextrose and galactose. It is probable that these compounds are similarly constituted to the glucosides, and they are respectively named *glucosidogalactose*, *galactosidodextrose*, and *galactosidogalactose*. They yield phenylosazones which are relatively readily soluble in water. Top yeasts do not ferment the three disaccharides, and they may be freed from monosaccharides by the action of these yeasts. Bottom yeasts decompose glucosidogalactose and galactosidoglucose, but not galactosidogalactose. All three disaccharides are hydrolysed by emulsin after contact for several days at 35°, but not by kephir lactase. Galactosidoglucose is probably identical with melibiose; its phenylosazone melts at 173—174° and the *p*-bromophenylosazone at 181°, both a few degrees lower than the corresponding compounds from melibiose.

Phenylglucosidogalactosazone melts at 175—177° (corr.); it is somewhat less soluble in benzene or toluene than galactosidoglucosazone.

Phenylgalactosidogalactosazone melts at 176—178° (corr.), is only sparingly soluble in chloroform, benzene, or toluene, and insoluble in ether or light petroleum. All three osazones yield osones when their aqueous solutions are boiled with benzaldehyde.

Kephir lactase partially converts solutions of pure galactose into a new disaccharide, iso*lactose*, the *osazone* of which crystallises in yellow needles melting at 193—196° (corr.). The sugar is not fermented by top, but is by bottom, yeasts, and is also hydrolysed by kephir lactase.
J. J. S.

Isomeric Acetohalogen Derivatives of Sugars and Synthesis of Glucosides. III. By EMIL FISCHER and E. FRANKLAND ARMSTRONG (*Ber.*, 1902, **35**, 3153—3155. Compare Abstr., 1901, i, 257, 671, and this vol., i, 263).—*β-Hepta-acetylbromomaltose*, $C_{26}H_{35}O_{17}Br$, obtained by the action of dry liquid hydrogen bromide on octa-acetylmaltose in sealed tubes at the ordinary temperature, crystallises from light petroleum in colourless prisms melting at 84° (corr.). It reacts with sodium phenoxide, yielding *hepta-acetylphenylmaltoside*, $C_{32}H_{40}O_{18}$, which melts at 157—158° (corr.) and is only sparingly soluble in hot water or dilute acids. On hydrolysis with barium hydroxide, it yields *β-phenylmaltoside*, $C_{12}H_{21}O_{10}\cdot OPh$, in the form of small, colourless prisms melting at 96° and with $[\alpha]_D$ +34·0° at 20°. *Tetra-acetylethylgalactoside* may be readily obtained by the action of ethyl alcohol on *β*-tetra-acetylchlorogalactose in the presence of silver carbonate; it melts at 88° (corr.) and has $[\alpha]_D$ −29·8° at 20°; on hydrolysis with barium hydroxide, it yields *β-ethylgalactoside* melting at 153—155° and with $[\alpha]_D$ −4·0° at 20°.

β-Methyl-, *β*-ethyl-, and *β*-phenyl-galactosides are hydrolysed by emulsin and also by kephir extract. J. J. S.

Optical Rotatory Power of Sucrose when dissolved in Amines. By GUY MAURICE WILCOX (*J. Physical Chem.*, 1902, **6**, 339—342).—It was found that rotation of sugar in solutions in allylamine, amylamine, and *iso*propylamine is considerably greater than in water. In amylamine and allylamine solution, the rotation was found to decrease with increasing concentration; in the case of *iso*propylamine solution, only one observation was made, so that the effect of concentration was not determined. L. M. J.

Isomerism of the β-Naphthylhydrazones of the Sugars. By WILLIAM ALBERDA VAN EKENSTEIN and CORNELIS A. LOBRY DE BRUYN (*Ber.*, 1902, **35**, 3082—3085. Compare Abstr., 1896, i, 588; 1897, i, 41).—The results recently obtained by Hilger and Rothenfusser (this vol., ii, 479) on the β-naphthylhydrazones of some sugars do not agree with the former observations of the authors (*loc. cit.*). This difference is due to the formation of stereoisomeric compounds. The *galactose-β-naphthylhydrazone* obtained by the authors melts at 167° and has $[\alpha]$ +24°, whilst that obtained by Hilger and Rothenfusser has $[\alpha]$ +10°. *Dextrose-β-naphthylhydrazone* has been obtained as a very soluble substance melting at 95° with $[\alpha]_{\text{Auer}}$ +40°; as a substance melting at 125°, and with lower rotatory power, and in a third form melting at 158—159° and having $[\alpha]_{\text{Auer}}$ +22°.

From lævulose, two isomeric β-naphthylhydrazones can be obtained according to the conditions. J. McC.

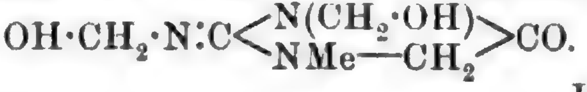
Synthesis of Carbohydrates and the Explanation of Natural Processes based thereon. By JULIUS WALTHER (*Chem. Zeit.*, 1902, **26**, 763—771. Compare this vol., ii, 203).—The author has confirmed his former observations (*loc. cit.*) and discusses their bearing on the physiological processes of plants and animals. K. J. P. O.

Reaction between Benzene and Cellulose. II. By A. M. NASTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 505—508. Compare this vol., i, 362).—The compound obtained by the action of benzene on a sulphuric acid solution of cellulose, which the author previously thought to be tetraphenylcellulose (*loc. cit.*), is now found to contain sulphur. The composition of the product when dried at the ordinary temperature in the desiccator is $C_{180}H_{134}O_{25}S_2$, whilst when dried at 105—110° it has the formula $C_{180}H_{128}O_{22}S_2$; these formulæ correspond with 6 mols. of tetraphenylcellulose + $2SO_2$, less 9 and $12H_2O$ respectively. The main product obtained on dry distillation of this compound is toluene, whilst when oxidised with potassium permanganate it yields benzoic acid; hence the phenyl groups present must be directly connected with carbon atoms.

T. H. P.

Crystalline Forms of Platinichlorides of the Aliphatic Amines. By A. RIES (*Zeit. Kryst. Min.*, 1902, **36**, 321—385).—Detailed crystallographic descriptions are given of the platinichlorides of the primary, secondary, and tertiary fatty amines and quaternary ammonium compounds, and of a few of the corresponding compounds containing bromine, iridium, or tin. The results are compared and discussed, especially with respect to their morphotropic relations.

L. J. S.

Action of Formaldehyde on Creatine and Creatinine. By Max Jaffé (*Ber.*, 1902, **35**, 2896—2901).—On treating a cold aqueous solution of creatine with dilute formaldehyde, no reaction takes place, but on heating, a *substance*, $C_6H_{11}O_3N_3,2H_2O$, separates in very long, colourless needles, which lose water at 100—105°, decompose at 250°, and are fairly soluble in water and other solvents; it does not react with the usual formaldehyde reagents. On benzoylating by the Schotten-Baumann method, a *dibenzoyl* derivative, $C_6H_9O_3N_3Bz_2$, is obtained as colourless needles melting at 265—266°. Creatinine yields the same substance on treatment with formaldehyde. It probably has the formula  $OH\cdot CH_2\cdot N{:}C<\begin{matrix}N(CH_2\cdot OH)\\ NMe—CH_2\end{matrix}>CO$.

K. J. P. O.

Reactions between Acid and Basic Amides in Liquid Ammonia. By Edward C. Franklin and Orin F. Stafford (*Amer. Chem. J.*, 1902, **28**, 83—107).—Franklin and Kraus (Abstr., 1900, ii, 382) have shown that a close analogy exists between liquid ammonia and water as electrolytic solvents, and that acid and basic amides bear a relation to liquid ammonia similar in many respects to that of ordinary acids and bases to water. From these considerations, it seemed probable that reaction would take place between an acid and a basic amide in liquid ammonia with the facility which marks the interaction of ordinary acids and bases in water. This has been found to be the case by means of a large number of experiments carried out in a specially devised apparatus.

Potassamide is very soluble in liquid ammonia and separates from concentrated solutions as a colourless, well crystallised, hygroscopic mass. When potassamide (1 mol.) and acetamide (1 mol.) are allowed to react in presence of liquid ammonia, hydrogen is evolved and crystals of *potassiumacetamide*, $CH_3\cdot CO\cdot NHK,nNH_3$, separate from the solution; this substance is also formed by the action of potassium on a solution of acetamide in liquid ammonia. When left in the air, the crystals lose their ammonia of crystallisation and become opaque. By the action of potassium amide (2 mols.) on acetamide (1 mol.), a *dipotassiumacetamide*, $CH_3\cdot CO\cdot NK_2$, is produced.

The *mono-* and *di-potassium* derivatives of benzamide, benzenesulphonamide, *m*-methoxybenzenesulphonamide, *p*-methoxybenzenesulphonamide, sulphamide, and carbamide, and the *mono-potassium* derivatives of phenylacetamide and *p*-toluenesulphonamide were also prepared. Benzoicsulphinide yields a *potassium* compound, probably

$$NHK\cdot CO\cdot C_6H_4\cdot SO_2\cdot NHK.$$

The reactions between potassamide and formamide, dichloroacetamide, thioacetamide, cyanoacetamide, *p*-chlorobenzamide, succinimide, thiocarbamide, allylthiocarbamide, picramide, and *m*-nitro-*p*-toluidine were also studied, but although in each case action evidently occurred, the products could not be isolated.

When sodamide (1 mol.) is brought in contact with acetamide (1 mol.) in solution in liquid ammonia, *sodiumacetamide*,

$CH_3CO\cdot NHNa,nNH_3$,

is produced; this compound is also formed by the action of sodium on a solution of acetamide.

Magnesium was found to react with acetamide, benzenesulphonamide, benzoicsulphinide, benzamide, phenylacetamide, cyanoacetamide, and cyanamide, whilst formamide, toluenesulphonamide, succinamide, and sulphamide were without appreciable action. *Magnesium-acetamide*, *-benzenesulphonamide*, and *-cyanamide* were prepared and analysed.

Magnesium, sodium, and potassium readily react with solutions of ammonium salts; when magnesium is treated with solution of ammonium nitrate or bromide, magnesium nitrate or bromide separates from the solution. E. G.

Action of Mercuric Bromide on the Alkali Thiocyanates. By HERMANN GROSSMAN (*Ber.*, 1902, **35**, 2945—2946).—Mercuric bromide dissolves in solutions of the alkali thiocyanates forming two series of salts. One series contains one mol. of each constituent, the *ammonium* salt, $HgBr_2,NH_4SCN$, which crystallises in stable needles, being described. The other series contains two mols. of the thiocyanate to one mol. of mercuric bromide. The *ammonium* salt,

$HgBr_2,2NH_4SCN,H_2O$,

of this series is deliquescent, but the *potassium* salt, $HgBr_2,2KSCN$, is crystalline and stable in air. R. H. P.

Action of Ethyl Iodide on Potassium Stannite. By PAUL PFEIFFER (*Ber.*, 1902, **35**, 3303—3307).—When a strong alkaline solution of stannous hydroxide is boiled with ethyl iodide and alcohol, the resulting solution deposits tin diethyl oxide. The formation of this compound is probably due to the action of the alkali on the potassium ethylstannite at first formed according to the equation $2SnEtO\cdot OK = SnEt_2O + SnO_3K_2$. R. H. P.

Genesis of Naphthenes and Naphthenecarboxylic Acids. By OSSIAN ASCHAN (*Annalen*, 1902, **324**, 1—39).—The author's experimental results support the theory which assumes that the naphthenes and their carboxylic acids are secondary products of the distillation of mineral oil in the earth's interior, being formed by the polymerisation of compounds of the olefine series which result from the initial decomposition of fossil fat.

Although ethylene, when dissolved in carbon disulphide and treated with anhydrous aluminium chloride, does not, at the ordinary temperature, undergo any polymerisation, yet, under these conditions, the crude amylene derived from amyl alcohol gives rise to saturated hydrocarbons. The products of lowest boiling point contained in the fractions 32—35° and 35—40° consist chiefly of a saturated hydrocarbon, C_5H_{10}, closely resembling methyl*cyclo*butane.

The next fraction, 56—62°, contains a hexane, C_6H_{14}, which corresponds in boiling point with $\beta\gamma$-dimethylbutane or β-methylpentane. The addition of a methyl group to the amylene carbon chain by the action of aluminium chloride has hitherto not been observed.

The fraction 76—81° contains a saturated hydrocarbon, C_6H_{12}, corresponding in composition with *cylco*hexane.

The fraction 150—200° appears to consist of a mixture of paraffins, $C_{10}H_{22}$, $C_{11}H_{24}$, and $C_{12}H_{26}$.

When pure amylene (b. p. 37—39°) is employed in these experiments, the fraction 55—60° probably contains a branched chain hexane, whilst the fraction 260—265° consists chiefly of naphthenes mixed with small quantities of the paraffins $C_{15}H_{32}$.

The tarry residues of these fractionations, when distilled under diminished pressure, yield a hydrocarbon, $C_{38}H_{66}$, boiling at 190—220° under 30 mm. pressure.

In one series of experiments, *cyclo*hexane, when heated with fuming hydriodic acid at 300°, became converted into methyl*cyclo*pentane.

A negative result was obtained in a second series of experiments. *cyclo*Hexane also undergoes transformation when left in contact with anhydrous aluminium chloride.

It was not found possible to oxidise methyl*cyclo*pentane to a cyclic monocarboxylic acid; dibasic acids only were obtained, namely, succinic, adipic, and a trace of glutaric acid. In one case, *αα*-dimethylpropionic and *iso*valeric acids were identified, these products being probably due to the oxidation of the paraffins present in the methyl*cyclo*pentane.

When treated with dilute nitric acid, the cyclic hydrocarbon becomes oxidised to a mixture of acetic and succinic acids.

G. T. M.

Methyl*cyclo*hexenes and Methyl*cyclo*hexenones. By Otto Wallach (*Ber.*, 1902, **35**, 2822—2825).—Cyclic alcohols, when dehydrated with phosphoric oxide or zinc chloride, often form unsaturated ring hydrocarbons, which are isomerides of those which would be expected from the constitution of the alcohol. These isomerides form less soluble nitrosyl chlorides and nitrosates than the untransformed hydrocarbons.

The *tetrahydrotoluene*, obtained when 1-methyl*cyclo*hexan-3-ol is dehydrated by zinc chloride, differs from that previously described (Abstr., 1896, i, 310). It boils at 106—107°, has a sp. gr. 0·799, n_D 1·44234 at 20°, and α_D +17°45′ in a 1 dcm. tube. The *nitrosate* reacts with piperidine forming the *nitrolepiperidide*, which is a beautifully crystalline compound melting at 152—153°. When the nitrosate is warmed with alcoholic potash, a liquid *methyl*cyclo*hexenoneoxime*, $C_7H_{10}\colon NOH$, is obtained, which, when hydrolysed with sulphuric acid, yields a *methyl*cyclo*hexenone*, $C_7H_{10}O$. This ketone boils at 179—181°, is soluble in water, has a sp. gr. 0·97, and n_D 1·4843 at 21°, forms a semicarbazone which melts at 207—208°, and therefore differs from the methyl*cyclo*hexenone described by Knoevenagel (Abstr., 1897, i, 606). The exact constitution of these compounds has not been determined.

R. H. P.

Action of Sulphur Chloride on Benzene. By Eduard Lippmann and Isidor Pollak (*Monatsh.*, 1902, **23**, 669).—If commercial benzene is warmed on a water-bath with 15 per cent. of sulphur chloride until the evolution of hydrogen chloride ceases (192 hours), and is then washed with dilute sodium hydroxide solution, and dried over calcium chloride, it distils at 81° and is free from thiophen. G. Y.

Organic Additive Compounds. By PAUL LEMOULT (*Compt. rend.*, 1902, **135**, 346—348).—1-Chloro-2 : 4-dinitrobenzene combines with tertiary bases of the diphenylmethane series to form coloured additive products.

The *compounds* $C_6H_3Cl(NO_2)_2,CH_2(C_6H_4{\cdot}NMe_2)_2$ and

$$C_6H_3Cl(NO_2)_2,CH_2(C_6H_4{\cdot}NEt_2)_2$$

crystallise in reddish-brown needles and melt at 72° and 42·5° respectively. 1-Chloro-2 : 4 : 6-trinitrobenzene and 4 : 4′-tetramethyldiaminodiphenylmethane give rise to the compound

$$C_6H_2Cl(NO_2)_3,CH_2(C_6H_4{\cdot}NMe_2)_2,$$

which separates in black flakes and melts at 71°. The 2 : 4-*dinitrophenoxide*, $OH{\cdot}C_6H_3(NO_2)_2,CH_2(C_6H_4{\cdot}NMe_2)_2$, separates in large, black crystals melting at 72° ; the *picrates*, $OH{\cdot}C_6H_2(NO_2)_3,CH_2(C_6H_4{\cdot}NMe_2)_2$ and $OH{\cdot}C_6H_2(NO_2)_3,CH_2(C_6H_4{\cdot}NEt_2)_2$, crystallise in yellow leaflets and melt respectively at 185° and 190°. Picramide gives rise to the *compound* $NH_2{\cdot}C_6H_2(NO_2)_3,CH_2(C_6H_4{\cdot}NMe_2)_2$, crystallising in lustrous, black leaflets and melting at 106°.

These substances are all readily dissociated into their generators even in their solutions in the organic solvents. G. T. M.

Nitroethylbenzene and its Tetrazo-dye. By GUSTAV SCHULTZ and J. FLACHSLÄNDER (*J. pr. Chem.*, 1902, [ii], **66**, 153—172. Compare Abstr., 1884, 902, and Beilstein and Kuhlberg, *Annalen*, 1870, **156**, 206).—*o*-Nitroethylbenzene melts at −23° and boils at 223—224°. *p*-Nitroethylbenzene melts at −32°, boils at 241—242°, and forms a *sodium sulphonate*, $NO_2{\cdot}C_6H_3Et{\cdot}SO_3Na,2H_2O$, which crystallises in long needles and is easily soluble in water.

Diaminodiethyldiphenyl, prepared from *o*-nitroethylbenzene (Schultz, *loc. cit.*), forms a *dihydrochloride*, $C_{16}H_{20}N_2,2HCl$, which crystallises in mother-of-pearl leaflets and is easily soluble in water or hot alcohol, and a *dibenzylidene* derivative, $C_{16}H_{16}N_2(CHPh)_2$, which crystallises from alcohol in yellow needles, melts at 124—125°, is easily soluble in hot alcohol, more sparingly so in cold alcohol or ether, and is hydrolysed by dilute mineral acids. The *dipicrate*, formed in alcoholic solution in presence of excess of picric acid, crystallises in glistening, golden leaflets, decomposes without melting at 225°, and on recrystallisation from alcohol is hydrolysed to the *monopicrate*, which separates in glistening, yellow needles, decomposes at 225—230°, and is only sparingly soluble in water or alcohol.

Benzidine forms a *dipicrate* which decomposes at 190°, is sparingly soluble in ether, but easily so in water or alcohol ; it is stable in absolute alcohol, but is completely hydrolysed to benzidine and picric acid on recrystallisation from aqueous alcohol, and more slowly on contact with aqueous alcohol in the cold. *Tolidine dipicrate* decomposes at 215°, is stable in absolute alcohol, and on recrystallisation from aqueous alcohol is hydrolysed, but more slowly than the benzidine salt. When left with aqueous alcohol in the cold, tolidine dipicrate is only partly hydrolysed, probably to the monopicrate. The mother liquor from the preparation of 4 : 4′-diamino-3 : 3′-diethyldiphenyl contains *o*-aminoethylbenzene and a *base* which is obtained as a thick syrup soluble in alcohol or ether, and may be 4-amino-3 : 2′-diethyldiphenylamine or, less probably, 2 : 4′-diamino-3 : 3′-diethyldiphenyl. It forms a *hydrochloride*, $C_{16}H_{20}N_2,2HCl$, which crystallises in leaflets from alcohol, in which it is sparingly soluble, a *benzylidene* derivative, $C_{16}H_{18}N_2{:}CHPh$, which crystallises in glistening leaflets, melts at 110—112°, and is soluble in alcohol or benzene, and a *picrate*, $C_{16}H_{20}N_2,C_6H_3O_7N_3$, which crystallises from alcohol in golden-yellow leaflets, decomposes at 235—240°, and is only sparingly soluble in water or alcohol. With ferric chloride in dilute hydrochloric acid solution, the base gives a blue-green coloration, which disappears on addition of concentrated hydrochloric acid.

When diazotised with 2 mols. of sodium nitrite and coupled with α-naphthylamine-4-sulphonic acid, benzidine, *o*-tolidine, and diaminodiethyldiphenyl yield similar dyes (sodium salts). The reaction takes place most easily with benzidine, least easily with diaminodiethyldiphenyl. The new dye forms green, glistening crystals and is less soluble in water and more stable towards light and acetic acid than the dye derived from *o*-tolidine, which is also less soluble and more stable than the benzidine dye.

Of the dyes (sodium salts) obtained by coupling with β-naphthylamine-6-sulphonic acid, that derived from benzidine is insoluble in water, those from *o*-tolidine and diaminodiethyldiphenyl are soluble. Dyes have also been obtained by coupling diazotised diaminodiethyldiphenyl with salicylic acid and with 8-amino-α-naphthol-3 : 6-sulphonic acid. G. Y.

Study of Bisnitrosylbenzyl and the Bye-products obtained in its Formation. By WILHELM BEHRENS and ROBERT BEHREND (*Annalen*, 1902, **323**, 265—278. Compare Bamberger and Renauld, Abstr., 1898, i, 20; Bamberger and Szolayski, Abstr., 1901, i, 84).—The compound obtained as a bye-product in the preparation of bisnitrosylbenzyl by oxidising β-benzylhydroxylamine with chromic acid is benzaldoxime anhydride, $(C_6H_5{\cdot}CH{\cdot}N)_2O$, corresponding in its properties with the substance produced by the aërial oxidation of the same hydroxylamine derivative. In the former reaction, the anhydride is accompanied by an oily mixture of benzaldehyde, benzyl benzoate, and benzonitrile (?).

Bisnitrosylbenzyl, when dissolved in chloroform and treated with hydrogen chloride, undergoes a complicated change, giving rise to benzoylhydrazine, benzoylbenzylidenehydrazine, hydrazine, benzyl chloride, benzaldehyde, tarry products, and probably a trace of benzonitrile.

Bisnitrosylbenzyl is scarcely attacked by bromine in hot chloroform solution and is not affected by permanganate solution; with nitric acid, it yields a mixture of nitrobenzoic acids. G. T. M.

Electrolytic Oxidation of Naphthalene. By A. PANCHAUD DE BOTTENS (*Zeit. Elektrochem.*, 1902, **8**, 673—675).—When a cold solution of naphthalene in a mixture of acetone and sulphuric acid is electrolysed, some *a*-naphthaquinone is formed at the anode and a considerable quantity of a brown, non-crystalline substance. Naphthalene-*a*-sulphonic acid or its sodium salt and 1-amino-*β*-naphthol-4-sulphonic acid, dissolved in water or a mixture of acetone and sulphuric acid, gave small quantities of phthalic acid. T. E.

Halogen-substituted Dinitronaphthalenes. By Fritz Ullmann and Fortunato Consonno (*Ber.*, 1902, **35**, 2802—2811).—5-Bromo-*a*-naphthylamine, obtained by reducing Guareschi's 5-bromo-*a*-nitronaphthalene with stannous chloride, melts at 69° and yields an *acetyl* derivative crystallising in pale pink, twinned needles and melting at 215°.

5-Bromo-1 : 8-dinitronaphthalene is produced by nitrating 5-bromo-*a*-nitronaphthalene or *a*-bromonaphthalene; when heated with alcoholic ammonia, it yields 4 : 5-*dinitro-a-naphthylamine*, which separates from glacial acetic acid in reddish-brown crystals melting at 243°. 4 : 5-*Dinitro-a-naphthylmethylamine* is produced in a similar manner by the use of methylamine; it forms brick-red crystals and decomposes at 259°. 4 : 5-*Dinitro-a-naphthyldimethylamine*, prepared by the interaction of 5-bromo-1 : 8-dinitronaphthalene and dimethylamine, crystallises in dark red needles and melts at 176°.

4 : 5-Dinitro-*a*-naphthol, resulting from the action of sodium carbonate solution under pressure on the bromonitro-compound, decomposes at 208°. Friedländer gives the decomposition temperature as 230° (compare Abstr., 1900, i, 150).

4 : 5-*Dinitronaphthyl methyl ether*, produced by heating 5-bromo-1 : 8-dinitronaphthalene with an alcoholic solution of sodium methoxide, separates from ether in yellow, feathery crystals melting at 216°.

4 : 5-*Dinitronaphthyl ethyl ether* crystallises in nacreous leaflets and melts at 182° (compare Heermann, Abstr., 1891, 1379.)

8-Chloro-*a*-nitronaphthalene, the product of the action of chlorine on *a*-nitronaphthalene in the presence of ferric chloride, on reduction, yields 8-chloro-*a*-naphthylamine which melts at 89° and gives an *acetyl* derivative crystallising in colourless needles and melting at 137°.

4-Chloro-1 : 5-dinitronaphthalene, melting at 138°, results from the nitration of the preceding nitro-compound; it yields 4 : 8-*dinitro-a-naphthylamine* when heated with alcoholic ammonia, this product crystallising in brick-red needles and decomposing at 197°. 4 : 8-Dinitro-*a*-naphthol, produced from the corresponding bromodinitro-compound by the action of sodium carbonate solution at 135°, melts at 235°, not at 135° as formerly stated. G. T. M.

Constitution of Primary Dinitrohydrocarbons. By Roland Scholl (*J. pr. Chem.*, 1902, [ii], **66**, 206—207. Compare Ponzio, this vol., i, 334).—The author draws attention to his observations on the reduction of diphenyldinitromethane (Abstr., 1891, 315). Ponzio's suggestion that, in the fatty dinitro-compounds, only one nitrogen atom is attached to carbon, has been made before but can no longer be maintained (compare Abstr., 1896, i, 198; 1901, i, 495). G. Y.

Tervalent Carbon. IV. By Moses Gomberg (*J. Amer. Chem. Soc.*, 1902, **24**, 597—628. Compare Abstr., 1901, i, 78).—When a solution of iodine is added to triphenylmethyl or one of its additive products, dissolved in an appropriate solvent, 80 per cent. of the theoretical yield of triphenyliodomethane is formed (*loc. cit.*). When the solvent is petroleum, the substance separates in yellow prisms which melt at 131—132° and are soluble in benzene, carbon disulphide and hot ethyl acetate, but insoluble in ether. It reacts like the corresponding bromo- and chloro-derivatives when treated with water, alcohol, and metals; and like them forms coloured additive compounds with the chlorides of tin, zinc, and antimony. With ammonia and amines, triphenyliodomethane also reacts in the usual manner, furnishing with ammonia, triphenylaminomethane; with ethylamine, triphenylmethylaminomethane; and with aniline, toluidine, &c., similar derivatives.

When the amount of iodine calculated for the formula CPh_3I,I_5 is added to a solution of triphenyliodomethane prepared as already described, there separates a penta-iodide of the above formula as dark blue, lustrous needles which melt at 90°. With sodium thiosulphate, only the "external" iodine is attacked with the formation of triphenyliodomethane and ultimately triphenylcarbinol. Alcohol converts the penta-iodide into triphenylmethane, but if the hydrogen iodide first formed be removed by addition of zinc dust, triphenylcarbinyl ethyl ether is obtained. Zinc dust, when added to neutral solutions of the periodide, furnishes triphenylmethyl.

Triphenylbromomethane penta-iodide, CPh_3Br,I_5 (compare Abstr., 1899, i, 155), prepared by addition of the calculated quantity of iodine to solutions of triphenylbromomethane, separates as an oil which becomes crystalline in a few seconds. It is slightly soluble in benzene or carbon disulphide, but readily so in ether. Its reactions are similar to those of the preceding compound.

The author points out that the results recorded in this and previous papers are all in favour of the view that the hydrocarbon which he has named triphenylmethyl has the constitution CPh_3 in which carbon is tervalent. T. A. H.

Dibenzylanthracene. By Eduard Lippmann and Isidor Pollak (*Monatsh.*, 1902, **23**, 672—679).—5 : 10-Dibenzylanthracene, prepared by heating anthracene with benzyl chloride and zinc dust in carbon disulphide solution, crystallises from benzene in glistening, whitish-yellow needles, melts at 239—240°, has a sp. gr. 0·1787 at 16°, and is only sparingly soluble in benzene, ether, carbon disulphide, or glacial acetic acid, and insoluble in alcohol or light petroleum. On oxidation with chromic acid in glacial acetic acid solution, it gives an almost quantitative yield of anthraquinone melting at 273°. On bromination in carbon disulphide solution, dibenzylanthracene yields a *bromo*-derivative, $CH_2Ph\cdot C_{14}H_8\cdot CHBrPh$, which crystallises in glistening, yellow leaflets, commences to lose hydrogen bromide at 160°, and melts at 187°. It is easily soluble in benzene or carbon disulphide, but only sparingly so in alcohol or ether. When boiled with water containing potassium carbonate or with glacial acetic acid, it is converted into hydroxydibenzylanthracene, $CH_2Ph\cdot C_{14}H_8\cdot CHPh\cdot OH$, which forms yellow crystals, melts at 225—226°, and is easily soluble in ether, benzene, or carbon disulphide, but only sparingly so in alcohol. The *ethyl* ether crystallises in soft leaflets, melts at 218°, and forms a fluorescent solution in benzene. G. Y.

Hexaphenylethane. By FRITZ ULLMANN and W. BORSUM (*Ber.*, 1902, **35**, 2877—2881).—On attempting to prepare triphenylmethane by the reduction of triphenylmethyl chloride with zinc in acetic acid solution, *hexaphenylethane*, $CPh_3{\cdot}CPh_3$, was formed; when the reduction was carried out with zinc and stannous chloride in acetic acid solution in the presence of hydrochloric acid, the yield amounted to 60—70 per cent. The hydrocarbon can be also obtained by reducing triphenylcarbinol in a similar manner. It forms small, colourless crystals, soluble in benzene or toluene, which melt at 231° (corr.), and boil at a higher temperature than sulphur. It is oxidised by chromic acid only with great difficulty, yielding triphenylcarbinol; by nitric acid, it is converted into a hexanitro-derivative, which melts at 265°. When the reduction of triphenylmethyl chloride is carried out in the complete absence of water, only the triphenylmethyl peroxide (m. p. 185°) prepared by Gomberg (Abstr., 1901, i, 77) is obtained. K. J. P. O.

Action of Ethylene Dibromide on *p*-Nitrosodimethylaniline. By HENRY A. TORREY (*Amer. Chem. J.*, 1902, **28**, 107—121).—When *p*-nitrosodimethylaniline is heated with an excess of ethylene dibromide, di-*p*-nitrosodimethylaniline-ethylene and *p*-nitrosodimethylaniline hydrobromide are produced.

Di-p-nitrosodimethylaniline-ethylene,

$$NO{\cdot}C_6H_4{\cdot}NMe_2{:}CH{\cdot}CH{:}NMe_2{\cdot}C_6H_4{\cdot}NO,$$

crystallises from amyl alcohol in deep red needles, decomposes at 230—240°, and is soluble in chloroform or glacial acetic acid; the *picrate* melts and decomposes at about 155°. If *p*-nitrosodimethylaniline is heated with an alcoholic solution of ethylene dibromide, the red ethylene derivative first formed suffers decomposition with production of tetramethyldiaminoazobenzene; the same compound is obtained when the red ethylene derivative itself is heated with *p*-nitrosodimethylaniline and alcohol. When the ethylene derivative is treated with dilute nitric acid, decomposition occurs with formation of formic acid, *p*-nitrosodimethylaniline *nitrate*, which melts and decomposes at 162°, and a *substance* which crystallises in yellow plates, melts at 255—256°, and does not contain oxygen.

p-Nitrosodimethylaniline *hydrobromide* forms yellow crystals and decomposes at 207°. The *platinichloride* obtained by the action of platinic chloride on an alcoholic solution of the hydrochloride differs from the two platinum salts described by Schraube (*Ber.*, 1875, **8**, 616). The *picrate* decomposes at about 140°. E. G.

Influence of the Solvent on the Orientation of the Isomerides obtained on Nitration in the Aromatic Series. By CARL SCHWALBE (*Ber.*, 1902, **35**, 3301—3303).—A preliminary note on the influence of the solvent during the nitration of ring compounds. Benzylideneaniline, when nitrated in concentrated sulphuric acid solution with nitric acid at 5°, yields *p*-nitroaniline only, but in glacial acetic acid solution with nitric acid and acetic anhydride gives rise to a mixture of *p*- and *o*-nitroaniline (see Pictet and Genequand, this vol., i, 584). R. H. P.

isoValeryl *p*-toluidide and *m*-Bromoisovaleryl-*p*-toluidide. By Francesco Maffezzoli (*Chem. Centr.*, 1902, ii, 504—505; from *Boll. Chim. Farm.*, **41**, 458—459).—iso*Valeryl*-p-*toluidide*,

$C_6H_4Me \cdot NH \cdot CO \cdot CH_2 \cdot CHMe_2$,

prepared by the action of phosphorus trichloride on a mixture of *p*-toluidine and *iso*valeric acid, crystallises from a large volume of boiling water in colourless, monoclinic plates, has a slight odour of valeric acid, melts at 98°, and is very readily soluble in alcohol, ether, chloroform, or benzene, but only slightly so in cold water. The m-*bromo*-derivative forms small, colourless, needle-shaped crystals, is odourless, melts at 95°, and is very readily soluble in alcohol, ether, or benzene, but only slightly so in water; on hydrolysis, it forms *m*-bromo-*p*-toluidine melting at 26°. E. W. W.

Production of Acylamines. By Frederick L. Dunlap (*J. Amer. Chem. Soc.*, 1902, **24**, 758—763).—When 2 gram-mols. of sodium acetate are intimately mixed with 1 gram-mol. of aniline hydrochloride and the mixture is heated in sealed tubes at 165° for three hours, 71—72 per cent. of the theoretical yield of acetanilide is obtained. Variations in proportion of reacting ingredients or of temperature or time of heating diminishes the yield, as does also the substitution of calcium acetate for the sodium salt. By the same reaction, with appropriate reagents, acetyltoluidide, acetamide, benzoylanilide, benzamide, and methylbenzamide have been prepared, but formanilide could not be obtained by the action of sodium formate on aniline hydrochloride at 185°. T. A. H.

Action of Phenylcarbimide on the Esters of some Oxy-acids. II. By Eugène Lambling (*Bull. Soc. Chim.*, 1902, [iii], **27**, 871—875. Compare this vol., i, 537, 603).—On heating together, at 175—178°, ethyl diethylglycollate and phenylcarbimide, the *phenylurethane* of *ethyl diethylglycollate*, $NHPh \cdot CO \cdot O \cdot CEt_2 \cdot CO_2Et$, is obtained, which crystallises from aqueous alcohol in slender needles melting at 68°; it is soluble in ether, chloroform, or benzene. On saponification with sodium hydroxide, it yields *diethyloxalanilide*, which crystallises in lozenge-shaped plates melting at 91°. Similarly, by heating ethyl benzilate with phenylcarbimide, there is obtained the *phenylurethane* of *ethyl benzilate*, $NHPh \cdot CO \cdot O \cdot CPh_2 \cdot CO_2Et$; it crystallises in slender, white needles, melts at 151° and is soluble in alcohol, ether, chloroform, or benzene. On boiling with excess of a solution of sodium hydroxide, it yields *benzilanilide*, which crystallises in microscopic prisms melting at 174—175°; it is insoluble in water, but soluble in alcohol, ether, chloroform, or benzene. The *phenylurethane* of *methyl salicylate*, obtained by heating methyl salicylate with phenylcarbimide, crystallises in white, microscopic needles melting at 96°. On saponification with sodium hydroxide, there is obtained *salicylanilide*, which crystallises in slender needles melting at 135°.

A. F.

Some Derivatives of β-Naphthylamine. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1902, [iii], **27**, 882—888).—*Ethyl-β-naphthylamine camphorsulphonate*, formed by the direct union of the acid and base dissolved in ethyl acetate, forms white, compact crystals melting at 117°; it dissolves in water but undergoes hydrolytic dissociation. *Diethyl-β-naphthylamine hydriodide*, crystallised from a mixture of ethyl acetate and alcohol, forms hard, colourless prisms melting at 152—153°. *Diethyl-β-naphthylamine*, obtained by the action of alkali on the hydriodide, is an almost colourless liquid boiling at 318—319°; a dilute ether or benzene solution exhibits a slight violet fluorescence. The *hydrochloride* forms deliquescent crystals melting at 177—178°. The *camphorsulphonate* could be obtained only as a gelatinous residue which refused to crystallise.

Triethyl-β-naphthylammonium iodide, obtained by heating diethylnaphthylamine with a slight excess of ethyl iodide, crystallises in colourless, lustrous, striated, rectangular plates melting at 174° *Trimethyl-β-naphthylammonium iodide*, prepared by the repeated action of methyl iodide on β-naphthylamine, crystallises in colourless plates melting at 190° with intumescence. *Dimethyl-β-naphthylamine* was obtained by distilling the quaternary base obtained from the iodide by the action of silver hydroxide; it forms a crystalline mass which melts at 46° and boils at 304·5—305°. *Dimethyl-β-naphthylamine hydrochloride* forms a felted mass of white, slender needles or colourless, non-deliquescent prisms melting at 159°. The *camphorsulphonate* forms colourless laminæ melting at 115°. A. F.

Preparation of Aminohydroxyphenanthrenes. By JULIUS SCHMIDT, and, in part, with A. KÄMPF (*Ber.*, 1902, **35**, 3129—3133. Compare Pschorr, this vol., i, 672).—9-Amino-10-hydroxyphenanthrene may readily be obtained by the reduction of phenanthraquinonemonoxime with hydrogen sulphide, and isolated as its hydrochloride. When the hydrochloride is boiled with acetic anhydride, it yields *anhydroacetyl*-9-*amino*-10-*hydroxyphenanthrene*, $C_{14}H_8$:NAc, in the form of yellowish, glistening needles, melting at 146—147° and dissolving in dilute mineral acids to deep blue solutions. The mother liquor from this anhydro-base yields Pschorr's 9-acetylamino-10-acetoxyphenanthrene.

Di-9-*hydroxyphenanthryl*-10-*amine*, $(OH\cdot C_{14}H_8)_2NH$, is obtained when water is added to an alcoholic solution of the base produced by the reduction of phenanthraquinonemonoxime with hydrogen sulphide; it crystallises in glistening, brown prisms melting and decomposing at 168—170°.

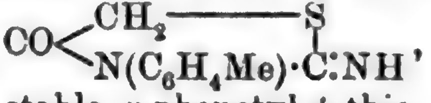
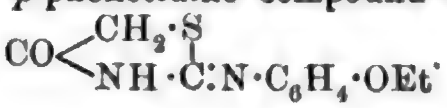
3-*Nitro*-10-(or 9-)-*amino*-9-(or 10-)-*hydroxyphenanthrene*, obtained by the reduction of 3-nitrophenanthraquinonemonoxime with alcoholic hydrogen sulphide, yields a *hydrochloride* crystallising in yellow needles. On treatment with aqueous solutions, it is converted into 3-nitro-9 : 10-dihydroxyphenanthrene.

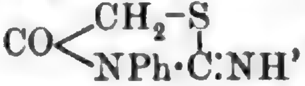
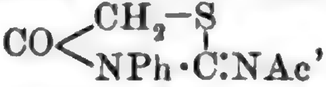
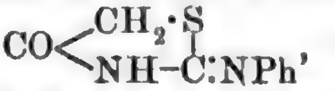
A small amount of 3 : 10-(or 9-)-*diamino*-9-(or 10-)-*hydroxyphenanthrene* may be obtained when the nitroquinonemonoxime is very carefully reduced with stannous chloride. It forms reddish-yellow needles melting at 264—265°. J. J. S.

Nitration of 2-Aminofluorene. By OTTO DIELS, EMIL SCHILL, and STANLEY TOLSON (*Ber.*, 1902, **35**, 3284—3290).—2-Acetylaminofluorene (Strassburger, Abstr., 1884, 754), when nitrated in acetic acid solution, gives a mixture of two mononitro-compounds which it has not been possible to separate. On saponification, a mixture of two nitroaminofluorenes is obtained which can be separated on account of their different basicities. The less basic one, 1-*nitro*-2-*aminofluorene*, $NH_2\cdot C_{13}H_8\cdot NO_2$, melts at 206° (corr.), and is comparatively insoluble in alcohol, ether, or benzene, but soluble in acetic acid. It forms a hydrochloride which, however, suffers hydrolysis in water. When reduced with zinc and hydrochloric acid, it gives 1 : 2-*diaminofluorene*, which is a monoacidic base forming the hydrochloride $C_{13}H_{12}N_2,HCl$. The free base can be obtained from the hydrochloride by means of methylamine; it forms white crystals which melt at 193° (corr.), and an alcoholic solution becomes green when treated with ferric chloride. With diacetyl, the diamino-compound forms a quinoline derivative of the formula $C_{17}H_{14}N_2$, which crystallises in long, colourless needles.

The more basic nitro-compound, 7-*nitro*-2-*aminofluorene*, crystallises in orange-red prisms, melts at 232° (corr.), and is easily soluble in alcohol or acetic acid. When reduced with zinc and hydrochloric acid, it gives 2 : 7-diaminofluorene (Schultz, Abstr., 1880, 814). J. McC.

Molecular Rearrangement of Thiocyanoacetanilides into Labile ψ-Thiohydantoins, and the Molecular Rearrangement of the Latter into Stable Isomerides. By HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1902, **28**, 121—158).—By the action of potassium thiocyanate on chloroacetanilides, Grothe (Abstr., 1901, i, 80) obtained a series of compounds which he believed were thiocyanoacetanilides, $NHR\cdot CO\cdot CH_2\cdot SCN$. Frerichs and Beckurts (Abstr., 1901, i, 80) repeated his experiments, and came to the conclusion that all his compounds, with the exception of the supposed thiocyanoaceto-*p*-toluidide, were normal thiocyanates; they found however, that by the action of potassium thiocyanate on an alcoholic solution of chloroaceto-*p*-toluidide for only a short time, a labile compound, which they regarded as thiocarbiminoaceto-*p*-toluidide, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot NCS$, was produced; they further observed that when the solution was warmed, this labile compound was rapidly converted into a substance supposed to be thiocyanoaceto-*p*-toluidide, and that the latter was quickly changed into *p*-tolylthiohydantoin.

The present authors have prepared the thiocyanoacetanilides according to Grothe's directions, and have found that although the aniline, *o*-toluidine, and *p*-xylidine compounds are correctly described, the so-called thiocyanoaceto-*p*-toluidide and thiocyanoacetyl-*p*-phenetidide are neither thiocyano- nor thiocarbimino-derivatives; the *p*-toluidine compound is a labile ψ-thiohydantoin,  $CO<\begin{array}{l}CH_2\text{———}S\\ N(C_6H_4Me)\cdot C{:}NH\end{array}$, whilst the *p*-phenetidine compound is the stable *p*-phenetyl-ψ-thiohydantoin,  $CO<\begin{array}{l}CH_2\cdot S\\ NH\cdot C{:}N\cdot C_6H_4\cdot OEt\end{array}$. The molecular rearrangement of thiocyanoacetanilides into the stable hydantoins does not involve the formation of a thiocarbimino-derivative at any stage.

Thiocyanoacetanilide crystallises in colourless, acicular prisms and melts at about 91°; if recrystallised from alcohol, it melts at 86—88°, and when crystallised from benzene it contains benzene of crystallisation which is rapidly lost on heating or on exposure to the air. By the action of the calculated quantity of thioacetic acid on it, *acetylthioglycollanilide*, $SAc\cdot CH_2\cdot CO\cdot NHPh$, is produced, which crystallises from alcohol in colourless needles and melts at 97—98°; the same compound may be obtained by the action of sodium thioacetate on chloroacetanilide. In two experiments, in which thiocyanoacetanilide was heated with an excess of thioacetic acid, a *substance* (probably an acetyldithiourethane) was obtained which crystallises in slender needles and melts and decomposes at 192°; in other experiments, a *dithiourethane*, $NH_2\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NHPh$, was produced which crystallises in square plates, melts at 162°, and is converted by the action of alkali hydroxide into alkali thiocyanate and a salt of thioglycollanilide. When thiocyanoacetanilide is treated with sodium hydroxide, phenylthiohydantoic acid is formed melting at 185—190°. If thiocyanoacetanilide is heated for a few minutes at its melting point, it is converted into the labile *phenyl-ψ-thiohydantoin* (4-keto-2-imino-3-phenyltetrahydrothiazole),  $CO<\begin{matrix}CH_2-S\\ NPh\cdot \overset{|}{C}{:}NH\end{matrix}$, which crystallises from benzene in orthorhombic prisms [$a:b:c=0\cdot97:1:1\cdot35$] and melts at 148° to a blood-red liquid; its *hydrochloride* melts at 192—193° and the *picrate* at 180°. If the labile thiohydantoin is warmed with thioacetic acid, hydrogen sulphide is evolved and an *acetyl* derivative,  $CO<\begin{matrix}CH_2-S\\ NPh\cdot \overset{|}{C}{:}NAc\end{matrix}$, is produced which melts at 191—192°; the same compound may be obtained by the action of acetic anhydride on phenylthiohydantoic acid or on thiocyanoacetanilide. The labile thiohydantoin is dissolved by sodium hydroxide with formation of phenylthiohydantoic acid. When the labile thiohydantoin is heated to 165°, it is converted into the stable phenyl-ψ-thiohydantoin,  $CO<\begin{matrix}CH_2\cdot S\\ NH-\overset{|}{C}{:}NPh\end{matrix}$, which forms triclinic crystals [$a:b:c=1\cdot508:1:0\cdot859$; $\alpha=108°25'$, $\beta=113°15'$, $\gamma=96°35'$]; the *hydrochloride* melts at 203° and the *diacetyl* derivative at 161—162°. By the action of benzyl chloride on the sodium salt of the stable thiohydantoin, phenylbenzylthiohydantoin is produced melting at 124—125°.

Thiocyanoaceto-*o*-toluidide melts at 102—103° as stated by Grothe, but if warmed with ether for two hours or repeatedly crystallised from benzene it melts at about 109°. By the action of thioacetic acid, it is converted into an *acetyldithiourethane*,

$$NHAc\cdot CS\cdot S\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4Me,$$

which melts and decomposes at about 200°. Thiobenzoic acid reacts with thiocyanoaceto-*o*-toluidide to form *benzoylthioglycoll*-o-*toluidide*, which crystallises in long needles and melts at 141—142°. When thiocyanoaceto-*o*-toluidide is treated with alkali hydroxide, *o*-tolylcyanamide is produced. By heating thiocyanoaceto-*o*-toluidide for half-an-hour at 110°, *o*-tolylthiohydantoic acid is obtained together with the labile o-*tolyl-ψ-thiohydantoin*; the latter compound melts at 131—132° and is thereby converted into the stable *o*-tolyl-*ψ*-thiohydantoin described by Dixon (Trans., 1897, 71, 623). When the stable hydantoin is heated with acetic anhydride, a *diacetyl* derivative is formed melting at 91—92°. o-*Tolylthiohydantoic acid* crystallises in thin plates and melts and decomposes between 208° and 230°. *o*-Tolylthiocarbamide melts at 162°, and not at 155° as stated by Staats (Abstr., 1880, 386).

Thiocyanoaceto-p-*toluidide*, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot SCN$, forms acicular prisms and melts at 85°. By the action of thioacetic acid, it is converted into a *dithiourethane*, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot S\cdot CS\cdot NH_2$. When heated above its melting point, labile p-*tolyl-ψ-thiohydantoin* is produced, which melts at 125—126°; its *acetyl* derivative crystallises in colourless plates and melts at 175—176°. If the labile thiohydantoin is treated with alkali hydroxide, *p*-tolylthiohydantoic acid is formed, which melts and decomposes at 210—212°. The stable *p*-tolyl-*ψ*-thiohydantoin, obtained by heating the labile form for a short time at a temperature near its melting point, crystallises in needles and melts at 183°; its *sodium* salt forms thin plates, and its *diacetyl* derivative crystallises in pale yellow prisms and melts at 163—164°.

Labile a-o-*xylyl-ψ-thiohydantoin* melts at 111°; by the action of thioacetic acid it is converted into the stable hydantoin melting at 179°. a-o-*Xylylthiohydantoic acid*, formed in the preparation of the labile hydantoin, melts and decomposes at about 208°.

Thiocyanoacetyl-*p*-xylidide,

$$C_6H_3Me_2\cdot NH\cdot CO\cdot CH_2\cdot SCN\ [Me : NH : Me = 1 : 2 : 4],$$

is converted by thioacetic acid into *acetylthioglycoll*-p-*xylidide*,

$$SAc\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3Me_2,$$

which crystallises in colourless prisms and melts at 139—140°. By the action of sodium hydroxide on thiocyanoacetyl-*p*-xylidide, p-*xylylcyanamide* is produced which melts at 118°. When thiocyanoacetyl-*p*-xylidide is boiled with ether for one to two hours, the labile p-*xylyl-ψ-thiohydantoin* is obtained, which crystallises in needles, melts at 109—110°, and is converted by alkali hydroxide into *p*-xylylcyanamide. p-*Xylylthiohydantoic acid*, $C_6H_3Me_2\cdot N(NH_2)\cdot CS\cdot CH_2\cdot CO_2H$, decomposes at about 200°, and when dissolved in alkali hydroxide yields *p*-xylylcyanamide. The stable *p*-xylyl-*ψ*-thiohydantoin crystallises in minute prisms and melts at 161—162°.

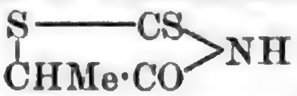
Labile p-*phenetyl-ψ-thiohydantoin* melts at 128° and is converted by thioacetic acid into the *acetyl* derivative, which crystallises in needles or prisms and melts at 155°. When the labile hydantoin is heated at 140—145° for half-an-hour, the stable *form* is produced which melts at 163—164°. p-*Phenetylthiohydantoic acid* melts and decomposes at 212°.

E. G.

Thiocyanates and *iso*Thiocyanates (Thiocarbimides). IV. By Henry L. Wheeler and Treat B. Johnson (*J. Amer. Chem. Soc.*, 1902, **24**, 680—690. Compare Abstr., 1902, i, 28, 537).—*β*-Bromo*iso*butane reacts with potassium thiocyanate to form *β-thiocyanoisobutane*, a colourless, pungent oil, which, with thioacetic acid, is converted into iso*butyl acetyldithiocarbamate*, $NHAc\cdot CS_2\cdot CMe_3$, forming yellow crystals melting at 112—113°, and a second substance crystallising in colourless plates from benzene.

a-Bromoisopropylbenzene, prepared by brominating the hydrocarbon at 115—120°, reacts with potassium thiocyanate to form ψ-cyanogen sulphide and an oil of unknown composition. *Diphenylbromoethane*, CPh_2BrMe, prepared by brominating the hydrocarbon at 100—105°, decomposes when heated in a vacuum into hydrogen bromide and diphenylethylene. The latter, together with ψ-cyanogen sulphide, is also produced by the action of potassium thiocyanate.

Methyl α-bromohydratropate, $CMePhBr\cdot CO_2Me$, prepared by brominating the ester at 150°, is an oil which decomposes when heated in a vacuum. It reacts with potassium thiocyanate forming an oil of unknown composition and ψ-cyanogen sulphide. The latter also results from the interaction of potassium thiocyanate and *tricarbethoxymethyl bromide*, a colourless oil, which boils at 162—165° under 16 mm. pressure and is obtained by brominating tricarbethoxymethane at 100°.

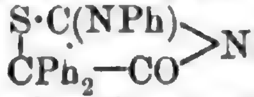
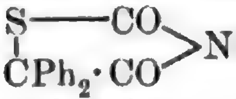
Ethyl bromomethylmalonate, when warmed with alcoholic potassium thiocyanate, yields *ethyl thiocyanomethylmalonate*, $NCS\cdot CMe(CO_2Et)_2$, a pungent oil which boils at 139—142° under 9 mm. pressure. With thioacetic acid in benzene solution, it furnishes 4-keto-2-thio-5-methylthiazolidine, 
$\left.\begin{array}{l}\mathrm{S{-\!\!-\!\!-}CS}\\ |\\ \mathrm{CHMe{\cdot}CO}\end{array}\right>\mathrm{NH}$

Ethyl phenylbromomalonate, $CPhBr(CO_2Et)_2$, obtained by brominating the ester at 140—150°, is a colourless oil which boils at 192° under 20 mm. and at 177—178° under 11 mm. pressure. With potassium thiocyanate, it yields *ethyl phenylthiocyanomalonate*, a colourless oil, which reacts with thioacetic acid to form 4-*keto-2-thio-5-phenylthiazolidine*. This crystallises in yellow prisms and melts at 178—179°.

Ethyl thiocyano*iso*butyrate reacts with thiobenzoic acid to form the *ethyl* iso*butyrate* derivative of *benzoyldithiocarbamate*,

$$NHBz\cdot CS_2\cdot CMe_2\cdot CO_2Et,$$

which crystallises from a mixture of petroleum and benzene in yellow prisms, melts at 113—114°, and dissolves readily in alcohol.

Ethyl diphenylchloroacetate, when treated with potassium thiocyanate, yields *ethyl diphenylthiocyanoacetate.* The latter does not react with thioacetic or thiobenzoic acids, but with aniline is converted into *triphenyl-ψ-thiohydantoin*, 
$\left.\begin{array}{l}\mathrm{S{\cdot}C(NPh)}\\ |\\ \mathrm{CPh_2{-}CO}\end{array}\right>\mathrm{NH}$, which crystallises from alcohol in colourless prisms and melts at 250°. This, with hydrochloric acid, is converted into 2 : 4-*diketo-5-diphenyltetrahydrothioazole*, 
$\left.\begin{array}{l}\mathrm{S{-\!\!-}CO}\\ |\\ \mathrm{CPh_2{\cdot}CO}\end{array}\right>\mathrm{NH}$, which crystallises in colourless prisms from alcohol and melts at 144—145°.

Ethyl phenylchloroacetate, when treated with phenylthiocarbamide, yields diphenyl-ψ-thiohydantoin identical with that previously obtained by the interaction of aniline and ethyl phenylthiocyanoacetate (*loc. cit.*). When treated with hydrochloric acid, the diphenyl-ψ-thiohydantoin furnishes 2 : 4-diketo 5 : 3-diphenyltetrahydrothioazole as white needles which melt at 173—174°. Benzylphenyl ψ-thiohydantoin (compare

Dixon, Trans., 1897, 71, 620) results when phenyl-ψ-thiohydantoin is treated with benzyl chloride in presence of sodium ethoxide, or when benzylphenylthiocarbamide is warmed with ethyl chloroacetate and therefore has the formula $\mathrm{CH_2}\left<\begin{matrix}\mathrm{S-C\cdot NPh\cdot CH_2Ph} \\ \| \\ \mathrm{CO\cdot N}\end{matrix}\right.$, which confirms that proposed by Dixon (*loc. cit.*) for the parent phenyl-ψ-thiohydantoin.

T. A. H.

Thiocyanates and *iso*Thiocyanates (Thiocarbimides). V. By HENRY L. WHEELER and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1902, **24**, 743—754. Compare Abstr., 1901, i, 514, and 1902, i, 28).—*Phenyl*-p-*tolylmethyl bromide*, $CMePhBr\cdot C_6H_4Me$, obtained by the action of dry hydrogen bromide on phenyl-*p*-tolylcarbinol at 100°, is a thin, red oil, which reacts in benzene solution with potassium thiocyanate to form *phenyl*-p-*tolylmethylthiocarbimide*, $C_6H_4Me\cdot CHPh\cdot NCS$, a mobile, reddish-coloured oil giving off irritating vapours. This reacts with thioacetic acid to form *phenyl*-p-*tolylmethylacetamide*,

$$NHAc\cdot CHPh\cdot C_6H_4Me,$$

which crystallises from ether in flat, rectangular prisms and melts at 129·5—131°. The thiocarbimide reacts with alcoholic ammonia, aniline, and β-naphthylamine to form respectively *phenyl*-p-*tolylmethylthiocarbamide*, $C_6H_4Me\cdot CHPh\cdot NH\cdot CS\cdot NH_2$, separating in rosettes of colourless needles which melt at 162—163°, *phenyl*-p-*tolylmethylphenylthiocarbamide*, $C_6H_4Me\cdot CHPh\cdot NH\cdot CS\cdot NHPh$, crystallising from alcohol in flat prisms which melt at 159°, and *phenyl*-p-*tolylmethyl-β-naphthylthiocarbamide*, $C_6H_4Me\cdot CHPh\cdot NH\cdot CS\cdot NH\cdot C_{10}H_7$, crystallising from alcohol in slender needles and melts at 170°.

p-*Benzyltolyl bromide*, prepared by brominating the hydrocarbon at 130—135°, is a heavy, yellowish oil which boils at 179—180° under 11 mm. pressure. Potassium thiocyanate converts it into the corresponding *thiocyanate*. This, however, with ammonia and β-naphthylamine, gives small quantities of the thiocarbamides described in the preceding paragraph.

Phenyl-a-naphthylmethyl bromide reacts with potassium thiocyanate to form the corresponding *thiocarbimide*, $C_{10}H_7\cdot CHPh\cdot NCS$, which crystallises in small plates melting at 76—77°. With thioacetic and thiobenzoic acids, respectively, this furnishes *phenyl-a-naphthylmethylacetamide*, $NHAc\cdot CHPh\cdot C_{10}H_7$, which crystallises in small needles and melts at 210°, and *phenyl-a-naphthylmethylbenzamide*,

$$NHBz\cdot CHPh\cdot C_{10}H_7,$$

which melts at 158°. The thiocarbimide reacts in the usual manner with ammonia and amines and the following thiocarbamides were thus prepared.

Phenyl-a-naphthylmethylthiocarbamide, $C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NH_2$, forming rectangular prisms which melt at 197—198°; *phenyl-a-naphthylmethylmethylthiocarbamide*, $C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NHMe$, crystallising in prisms which melt at 175—176°; *phenyl-a-naphthylmethyldiethylthiocarbamide*, $C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NEt_2$, forming flat prisms which melt at 112—113°; *phenyl-a-naphthylmethyldiisobutylthiocarbamide*,

$$C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot N(C_4H_9)_2,$$

which melts ~~at 142—~~143°; *phenyl-a-naphthylmethylphenylthiocarbamide*,

$C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NHPh$, forming colourless prisms which melt at 185°; *phenyl-a-naphthylmethylphenylmethylthiocarbamide*,

$$C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NHPhMe,$$

which melts at 182—183°; *phenyl-a-naphthylmethyl*-m-*chlorophenylthiocarbamide*, $C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NH\cdot C_6H_4Cl$, crystallising in acicular prisms which melt at 172—173°; *phenyl-a-naphthylmethyl*-m-*nitrophenylthiocarbamide*, $C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot NO_2$, forming light yellow prisms which melt at 191°; and *phenyl-a-naphthylmethyl-β-naphthylthiocarbamide*, $C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NH\cdot C_{10}H_7$, crystallising in needles which melt at 195°.

The thiocarbimide also reacts with phenylhydrazine to form *phenyl-a-naphthylmethylphenylthiosemicarbazide*, which melts first at 154°, then solidifies when further heated and remelts at 174—175°. After recrystallisation from alcohol, it melts at 178—179°. The transformation occurring is represented thus: $C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NPh\cdot NH_2 \rightarrow C_{10}H_7\cdot CHPh\cdot NH\cdot CS\cdot NH\cdot NHPh$ (compare Busch and Holzmann, Abstr., 1901, i, 234).

Di-a-naphthylmethane, $CH_2(C_{10}H_7)_2$, prepared by condensing naphthalene with chloromethyl acetate in presence of zinc chloride, when brominated at 135—145° furnishes *di-a-naphthylmethyl bromide*,

$$CH(C_{10}H_7)_2Br,$$

which crystallises from benzene in acicular prisms, melts at 181—182°, is readily soluble in chloroform, but less so in light petroleum. This reacts with potassium thiocyanate to form *di-a-naphthylmethylthiocarbimide*, $CH(C_{10}H_7)_2\cdot NCS$, which crystallises from alcohol in rectangular prisms and melts at 124—125°. With aniline, methylaniline, and naphthylamine, it reacts to form, respectively, *di-a-naphthylmethylphenylthiocarbamide*, $CH(C_{10}H_7)_2\cdot NH\cdot CS\cdot NHPh$, which crystallises in needles and melts at 225—226°; *di-a-naphthylmethylphenylmethylthiocarbamide*, $CH(C_{10}H_7)_2\cdot NH\cdot CS\cdot NPhMe$, forming needles which melt at 210—211°; and *di-a-naphthylmethyl-β-naphthylthiocarbamide*, $CH(C_{10}H_7)_2\cdot NH\cdot CS\cdot NH(C_{10}H_7)$, which crystallises in spherical masses of needles and melts at 218—219°.

Thiocyanoethylbenzene, $CHMePh\cdot SCN$, reacts with thioacetic acid to form the *ethylbenzene* derivative of *dithiocarbamic acid*,

$$NHAc\cdot CS_2\cdot CHPhMe,$$

which crystallises in slender, yellow prisms and melts at 99—100°.

With thiobenzoic acid, *iso*propyl thiocyanate forms *benzoyldithio*iso*propylcarbamate*, $NHBz\cdot CS_2Pr$. This crystallises in brilliant, yellow plates and melts at 74—75°.

Bromodinaphthaxanthone does not react with potassium thiocyanate, whence the author prefers for this substance the formula proposed by Werner (Abstr., 1902, i, 50) rather than that suggested by Fosse (Abstr., 1901, i, 604). T. A. H.

Thiocyanoacetic Acids and Thio-fatty Anilides. By HEINRICH BECKURTS and GUSTAV FRERICHS (*J. pr. Chem.*, 1902, [ii], 66, 172—193. Compare Abstr., 1900, i, 478; 1901, i, 80).—When boiled with water, carbaminethioglycollanilide yields thioglycollanilide and cyanic acid, the formation of carbon dioxide and ammonia being due to hydrolysis of the cyanic acid (compare Rizzo, Abstr., 1898, i, 659).

The formation of cyanic acid is determined by conversion into carbamide. The formation of diphenylcarbamide when carbaminethioglycollanilide is treated with aniline, and the formation of methylthioglycollanilide when the carbamine is heated with methyl iodide and sodium methoxide (Rizzo), are explained by the decomposition of the carbamine into thioglycollanilide and cyanic acid when warmed with alkalis or organic bases. The decomposition also takes place when the carbamine is heated above its melting point.

Thioglycollanilide melts at 111—112° (Rizzo, m. p. 105—107°) and is best obtained by warming the carbamine with alcoholic ammonia (compare Liebermann, *Annalen*, 1881, **207**, 129). A small part of the product is oxidised to dithiodiglycollanilide, which is insoluble in alcohol.

Grothe's compounds (Abstr., 1901, i, 80) are formed when chloroacetanilides are heated with potassium thiocyanate in alcoholic solution for 15 minutes. When chloroacetanilide is heated with potassium thiocyanate in alcoholic solution for several hours, phenylthiohydantoin (m. p. 178°) is formed (compare Rizzo, *loc. cit.*).

When warmed with fuming hydrochloric acid, the thiocyanoacetanilides are converted into carbaminethioglycollanilides. Thiocarbiminoacetylmethylanilide melts at 79° (Grothe, m. p. 69°), and is converted by fuming hydrochloric acid into *carbaminethioglycollmethylanilide*, $CN{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NMePh$, which crystallises in glistening leaflets and melts at 147°.

The following derivatives of the thio-fatty anilides are described. Dithiodiglycollanilide melts at 160—161° (Rizzo, m. p. 165°) and is best prepared by oxidation of thioglycollanilide with ferric chloride in alcoholic solution. Thioglycollanilide yields a *copper* derivative, $Cu_2(S{\cdot}CH_2{\cdot}CO{\cdot}NHPh)_2$, as an amorphous, yellow powder. *Ethylthioglycollanilide*, $SEt{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, prepared by the action of ethyl iodide and potassium hydroxide in alcoholic solution, forms colourless leaflets, melts at 61°, and is easily soluble in alcohol, but insoluble in water. *Dimethylmethylenedithioglycollanilide*, $CMe_2(S{\cdot}CH_2{\cdot}CO{\cdot}NHPh)_2$, formed by the action of hydrogen chloride on thioglycollanilide dissolved in acetone, crystallises from alcohol in colourless needles, melts at 170°, is soluble in hot, more sparingly so in cold, alcohol, and insoluble in water. Thiodiglycollanilide, formed by the action of potassium hydroxide on thioglycollanilide and chloroacetanilide in alcoholic solution, crystallises from alcohol in delicate needles and melts at 166—167° (Rizzo, *loc. cit.*, m. p. 160—161°; Anschütz and Biernaux, Abstr., 1893, i, 191, m. p. 168°). *Carboxyethylthioglycollanilide*, $CO_2Et{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, formed by the action of potassium hydroxide and ethyl chlorocarbonate on thioglycollanilide, crystallises from alcohol in flat, colourless needles and melts at 99°. *a-Carbaminethiolactanilide*,

$$NH_2{\cdot}CO{\cdot}S{\cdot}CHMe{\cdot}CO{\cdot}NHPh,$$

formed by the action of potassium thiocyanate on a-bromopropionic acid and aniline in alcoholic solution, crystallises in glistening leaflets, melts at 117°, and is easily soluble in alcohol, insoluble in water. *a-Thiolactanilide*, $SH{\cdot}CHMe{\cdot}CO{\cdot}NHPh$, formed by the action of ammonia on the carbamine, crystallises in colourless leaflets and melts at 91°. *a-Dithiodilactanilide*, $S_2(CHMe{\cdot}CO{\cdot}NHPh)_2$, obtained by oxidation of thiolactanilide with ferric chloride in alcoholic solution, crystallises in colourless needles and melts at 160°. The *copper* derivative, $Cu_2(S{\cdot}CHMe{\cdot}CO{\cdot}NHPh)_2$, forms a greenish-yellow powder. *a-Ethylthiolactanilide*, $SEt{\cdot}CHMe{\cdot}CO{\cdot}NHPh$, crystallises in colourless leaflets and melts at 97°. *a-Carbaminethiobutyranilide*, $NH_2{\cdot}CO{\cdot}S{\cdot}CHEt{\cdot}CO{\cdot}NHPh$, crystallises in colourless leaflets, melts at 120°, is easily soluble in alcohol, and insoluble in water. *a-Thiobutyranilide*, $SH{\cdot}CHEt{\cdot}CO{\cdot}NHPh$, crystallises in delicate, colourless needles and melts at 95°. *a-Dithiodibutyranilide*, $S_2(CHEt{\cdot}CO{\cdot}NHPh)_2$, crystallises from dilute alcohol in delicate, colourless needles and melts at 110°. The *copper* derivative, $Cu_2(S{\cdot}CHEt{\cdot}CO{\cdot}NHPh)_2$, forms a yellow, amorphous powder. *a-Ethylthiobutyranilide*, $SEt{\cdot}CHEt{\cdot}CO{\cdot}NHPh$, crystallises in delicate, colourless needles and melts at 68°. G. Y.

Hydroxamic Acids. By ANGELO ANGELI, FRANCESCO ANGELICO, and F. SCURTI (*Atti Real. Accad. Lincei*, 1902, [v], 11, i, 555—561). —The products of hydrolysis of most compounds, such as esters, amides, &c., are usually the same whether the decomposition is brought about by means of acids or alkalis, but with hydroxylaminesulphonic acids, benzenesulphohydroxamic, and nitrohydroxylaminic acids, this is not the case. Thus, with alkalis, these compounds yield a nitroxyl group and the corresponding acid, either sulphurous acid or a sulphinic acid, $RHSO_2$, and nitrous acid. With acids, however, the first two of the above compounds yield hydroxylamine together with sulphuric acid or a sulphonic acid, $R{\cdot}SO_3H$, whilst nitrohydroxylaminic acid loses immediately a mol. of water and gives nitrogen dioxide.

To obtain further information as to the mechanism of this hydrolytic action, the authors have prepared and studied hydroxamic acids of sulphur of the following types, which readily lend themselves to such decomposition: $R{\cdot}SO_2{\cdot}NH{\cdot}OH$; $R{\cdot}SO_2{\cdot}NR^1{\cdot}OH$; $R{\cdot}SO_2{\cdot}NH{\cdot}OR^1$; $R{\cdot}SO_2{\cdot}NR^1{\cdot}OR^2$; R representing an aliphatic or aromatic residue and R^1 and R^2 aromatic, aliphatic, or acid residues. The acids studied of the first type, namely, $C_{10}H_7{}^{a}{\cdot}SO_2{\cdot}NH{\cdot}OH$; $SO_2Et{\cdot}NH{\cdot}OH$; $C_6H_4(SO_2{\cdot}NH{\cdot}OH)_2$; and $C_{10}H_6(SO_2{\cdot}NH{\cdot}OH)_2$, which are analogous to the acid prepared by Piloty (Abstr., 1896, i, 555), behave similarly to benzenesulphohydroxamic acid. The alkaline hydrolysis was carried out in presence of either an aldehyde or nitrosobenzene, the nitroxyl group split off being thus converted into either a hydroxamic acid or nitrosophenylhydroxylamine. In the case, however, of a-naphthalenesulphohydroxamic acid, the residue, after the removal of nitroxyl, undergoes molecular rearrangement, yielding β-naphthalenesulphinic acid.

When sulphohydroxamic acids in which two atoms of hydrogen are replaced by acid radicles, for instance, $C_6H_5{\cdot}SO_2{\cdot}NAc{\cdot}OAc$ and $C_{10}H_7{\cdot}SO_2{\cdot}NAc{\cdot}OAc$, are hydrolysed in presence of alkali they exhibit a similar behaviour to the above. The same is the case with the acid, $C_6H_5{\cdot}SO_2{\cdot}NPh{\cdot}OH$, which yields benzenesulphinic acid and nitrosobenzene (corresponding with the nitroxyl residue) and with $C_6H_5{\cdot}SO_2{\cdot}N(CH_2Ph){\cdot}OH$, which gives nitrosotoluene, this soon undergoing transformation into benzaldehyde.

The above behaviour is explained by supposing that in alkaline solution these compounds react as if they possessed the tautomeric structure $R\cdot SO(OH){:}NOH$.

Substituted hydroxamic acids of the type $R\cdot SO_2\cdot NH\cdot OR^1$, where R^1 represents an alcoholic residue, do not, however, exhibit such a reaction. Thus the acid $C_6H_5\cdot SO_2\cdot NH\cdot O\cdot CH_2Ph$ can be precipitated unchanged from solution in alkali, even after long heating.

The authors have prepared dibenzenesulphohydroxamic acid, which they find to melt at 126°, although Koenigs (Abstr., 1878, 573) and Piloty (*loc. cit.*) gave the melting point 109°. With alkalis, this acid yields benzenesulphinic acid and nitrous acid, whilst with sulphuric acid it gives hydroxylamine. The corresponding naphthalene derivative, $OH\cdot N(SO_2\cdot C_{10}H_7{}^{\alpha})_2$, when treated with alkalis, likewise gives nitrous acid and a sulphinic acid, the latter being, however, the β-compound, namely, β-naphthalenesulphinic acid; if now the liquid be acidified, the latter acid reacts with the nitrous acid, giving di-β-naphthalenesulphohydroxamic acid, $OH\cdot N(SO_2\cdot C_{10}H_7{}^{\beta})_2$. The nitrous acid formed in this alkaline hydrolysis is obtained by the splitting off of water from the radicle $N(OH)_3$, so that in this case, as also in those given above, each sulphonic group attached to the nitrogen atom is replaced by a hydroxyl group.

This also happens in the alkaline hydrolysis of tribenzenesulphohydroxylamine, $(Ph\cdot SO_2)_3NO$, in which nitric acid is formed.

The analogy existing between the behaviour of these various compounds on alkaline hydrolysis is shown by the following scheme:

$$\begin{array}{lclcl}
(C_{10}H_7\cdot SO_2)HN\cdot OH & \longrightarrow & (OH)HN\cdot OH & \longrightarrow & NOH \\
(C_{10}H_7\cdot SO_2)_2N\cdot OH & \longrightarrow & (OH)_2N\cdot OH & \longrightarrow & NO_2H \\
(C_{10}H_7\cdot SO_2)_3NO & \longrightarrow & (OH)_3NO & \longrightarrow & NO_3H
\end{array}$$

T. H. P.

The Methyl Ethers of the True Nitrosophenols. *o*-Nitrosophenol. By ADOLF VON BAEYER and EDUARD KNORR (*Ber.*, 1902, **35**, 3034—3037).—The *o*- and *p*-nitrosoanisoles can readily be prepared by the action of Caro's reagent on the corresponding anisidines. p-*Nitrosoanisole* has not been obtained quite free from nitroanisole, but the impure compound crystallises in large, bluish-green prisms, melting at about 32—34°, forms bluish-green solutions in all organic solvents except light petroleum, readily volatilises in steam, and decomposes in the air. Dilute acids and alkalis readily hydrolyse it with formation of *p*-nitrosophenol. o-*Nitrosoanisole* is not accompanied by the nitro-compound and can readily be obtained pure; it crystallises in colourless, six-sided plates, melts at 103°, is stable in the air, dissolves to some extent in cold, and more readily in hot, water, forming green solutions, and is readily volatile in steam. It is only slowly attacked, even by concentrated aqueous potash, whilst acids convert it into a resinous mass.

o-*Nitrosophenol* (*o*-quinoneoxime), can be prepared from *o*-nitrosoanisole by gradually adding an aqueous solution of the latter to boiling aqueous potassium hydrogen sulphate. The free nitrosophenol has hitherto only been obtained as an oil. The *sodium* salt crystallises in dark red plates with a green surface lustre, and decomposes explosively when heated. The *barium* salt is sparingly soluble in water; the *silver* salt is a heavy, microcrystalline, almost black precipitate, which decomposes explosively when heated or brought into contact with a drop of sulphuric acid or fuming nitric acid. The properties of this *o*-nitrosophenol seem to indicate that it is an *o*-quinoneoxime.

A. H.

Nitrosophenol Dyes. I. By HERMANN DECKER and BASIL VON SOLONINA (*Ber.*, 1902, **35**, 3217—3225).—The blue compound formed by the action of fuming nitric acid on thymol ethyl ether (Kehrmann and Messinger, *Ber.*, 1901, **34**, 1626) was obtained in thin plates belonging to the rhombic system and melting constantly at 62—63°; it is formulated as an oxonium salt,

$$NO_3\cdot OHEt\cdot C_6H_2MePr\cdot NO\colon C_6H_2MePr\colon OEt\cdot NO_3,$$

two alternative formulæ being also given. When dissolved in chloroform, it passes into a red indophenol derivative,

$$OEt\cdot C_6H_2MePr\cdot N\colon C_6H_2MePr\colon O$$

or $OEt\cdot C_6H_2MePr\cdot NO\colon C_6H_2MePr\colon O$. This compound gives Liebermann's reaction with sulphuric acid, being thereby converted into a compound, $OH\cdot C_6H_2MePr\cdot N\colon C_6H_2MePr\colon O$.

The blue oxonium salt is reduced by sulphurous acid, hydrogen sulphide, or stannous chloride to *dithymolylamine diethyl ether*, $NH(C_6H_2MePr\cdot OEt)_2$; this separates from alcohol in beautiful, colourless crystals belonging to the triclinic system, melts at 70—71°, distils in part without decomposition, dissolves in acids, is not acted on by alkalis, and gives an intense indophenol reaction with concentrated sulphuric acid. The *hydrochloride*, $C_{24}H_{36}O_2NCl$, forms white needles and gradually oxidises in air to a red compound. *Thymoquinone thymoliminoether*, $OEt\cdot C_6H_2MePr\cdot N\colon C_6H_2MePr\colon O$, prepared by oxidising the preceding compound with ferric chloride, crystallises from alcohol, melts at 96—97°, has a dark red colour, is insoluble in water or alkalis, and dissolves in organic solvents with a deep violet-red colour. It is reduced by sulphurous acid, hydrogen sulphide, or stannous chloride to *dithymolylaminomonoethyl ether*,

$$OEt\cdot C_6H_2MePr\cdot NH\cdot C_6H_2MePr\cdot OH;$$

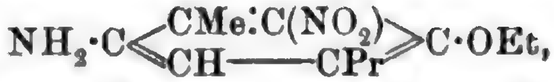
this was not isolated, but was hydrolysed, in the manner usual with an indophenol, to thymoquinone and an aminophenol sulphate. Hydrogen iodide reduces the indophenol ether in a similar manner to that just described, but also hydrolyses it to *dithymolylamine*, $NH(C_6H_2MePr\cdot OH)_2$; the *hydriodide* of this was obtained in colourless crystals; the *base* dissolves in alkalis to a colourless solution which is at once oxidised in the air and deposits dark blue, glistening crystals of a salt of *thymoquinonethymolimine*,

$$OH\cdot C_6H_2MePr\cdot N\colon C_6H_2MePr\colon O.$$

The series of changes here described proves the constitution of the dithymolylamine diethyl ether, and renders probable the formula assigned to the original blue salt.

T. M. L.

Partial and Complete Reduction Products of 2 : 6-Dinitrothymyl Ethyl Ether. By G. OTTO GAEBEL (*Ber.*, 1902, **35**, 2793—2802).—Ethyl-2 : 6-dinitrothymyl ether is most conveniently obtained by treating the silver derivative of 2 : 6-dinitrothymol with ethyl iodide in alcoholic solution.

2-*Nitro-6-aminothymyl ethyl ether*, 
$NH_2\cdot C\Big\langle\begin{matrix}CMe\colon C(NO_2)\\ CH\text{——}CPr\end{matrix}\Big\rangle C\cdot OEt$, produced by reducing the dinitro-compound either with alcoholic ammonium sulphide or with the calculated amount of stannous chloride in alcoholic solution, crystallises from this solvent in rhombic plates melting at 111—112°; the *hydrochloride* separates from dilute hydrochloric acid in white needles melting at 195° and decomposing at 200°; the *sulphate* forms white, silky needles; the *acetyl* and *benzoyl* derivatives separate from dilute alcohol in white needles and melt at 119° and 138° respectively. The amino-ether, when treated with bromine dissolved in carbon disulphide, yields a *bromo*-derivative crystallising from dilute alcohol or ether in yellow, rhombic plates melting at 75°. The *hydrochloride* separates in white needles on passing hydrogen chloride into the ethereal solution of the bromo-compound; it is dissociated by water and decomposes at 156°.

The *benzoyl* derivative, $OEt\cdot C_6MePr^\beta(NO_2)\cdot NHBz$, crystallises from dilute alcohol in white, quadratic plates and melts at 171°.

When 6-amino-2-nitrothymyl ethyl ether is diazotised with sodium nitrite and sulphuric acid in alcoholic solution, it yields an oily product which is probably a nitrothymyl ether, because, on reduction, it yields 2-*aminothymyl ethyl ether*, $OEt\cdot C_6H_2MePr^\beta\cdot NH_2$, which is characterised by means of its *hydrochloride*, a salt crystallising from dilute hydrochloric acid in white needles decomposing at 204°. The *platinichloride* forms reddish-yellow needles and decomposes at 169—170°; the *acetyl* derivative separates from dilute alcohol in white needles and the *benzoyl* derivative in white plates; the former melts at 109° and the latter at 144°.

The constitution of the preceding compounds was determined by comparing the above derivatives of the oily nitrothymyl ether with those of 6-nitrothymyl ethyl ether. The *hydrochloride, acetyl*, and *benzoyl* derivatives of the latter compound crystallise in white needles and melt respectively at 227—230°, 136°, and 151—152°; the amine reduces platinic chloride and hence the double salt was not obtained.

2 : 6-*Diaminothymyl ethyl ether hydrochloride*,

$$OEt\cdot C_6HMePr^\beta(NH_2HCl)_2,$$

resulting from the complete reduction of the corresponding dinitro-compound, separates from a mixture of concentrated hydrochloric acid, alcohol, and ether as a snow-white powder decomposing at 215°; the *tetra-acetyl* derivative crystallises from dilute alcohol in white flakes melting at 146°.

G. T. M.

Action of Benzaldehyde on Anisole. By W. Feuerstein and Andreas Lipp (*Ber.*, 1902, 35, 3252—3256).—When a mixture of anisole (2 mols.), benzaldehyde (1 mol.), and glacial acetic acid is added to well-cooled sulphuric acid containing some acetic acid, and after some time is poured on to ice, *phenyldianisylmethane*, $CHPh(C_6H_4\cdot OMe)_2$, separates out. It melts at 100—101° and is sparingly soluble in cold alcohol, but dissolves easily in concentrated sulphuric acid. It has been proved that the benzylidene group is in the *para*-position to the methoxy-groups because the same substance has been obtained by the methylation of 4 : 4′-dihydroxydiphenylmethane.

With *p*-tolyl methyl ether, a substance of the formula

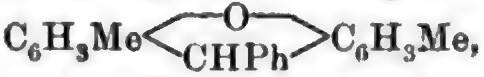
$$CHPh(C_6H_3Me{\cdot}OMe)_2\ [CHPh : Me : OMe = 1 : 3 : 5]$$

is formed which melts at 107—109° and is soluble in concentrated sulphuric acid to a violet solution.

The same condensation takes place with *p*-cresol, the *phenol*

$$CHPh(C_6H_3Me{\cdot}OH)_2\ [CHPh : Me : OH = 1 : 3 : 6]$$

being obtained; this melts at 158—160°, is soluble in the ordinary organic solvents and sulphuric acid, and gives a *diacetyl* derivative which melts at 121—122°. When subjected to distillation, this phenyldi-*p*-tolylmethane yields 1-*phenyl*-2 : 7-*dimethylxanthen*,



$$C_6H_3Me\left\langle\begin{matrix}O\\ CHPh\end{matrix}\right\rangle C_6H_3Me,$$

which crystallises in white, silky needles and melts at 191—191·5°; it is insoluble in alkalis but dissolves in concentrated sulphuric acid giving a green, fluorescent solution.

The condensation with *o*-tolyl methyl ether leads to a substance which melts at 101—102°, the constitution of which is probably $CHPh(C_6H_3Me{\cdot}OMe)_2$ [CH : Me : OMe = 1 : 3 : 4]. J. McC.

Dibenzylideneacetone and Triphenylmethane. By ADOLF VON BAEYER and VICTOR VILLIGER (*Ber.*, 1902, **35**, 3013—3033. Compare this vol., i, 380).—Trianisylmethane does not, as was at first believed, form coloured salts, and hence this substance, like triphenylmethane, is not halochromic, and the distinction between ammonium and oxonium salts, which was founded on the apparent halochromism of these substances, cannot therefore be maintained.

The properties of triphenylcarbinol in many respects differ from those of both alcohols and acids, and are more closely allied to those of aldehydes or ketones. A close analogy exists between the behaviour of the carbinol to many reagents and that of nitrous acid. The carbinol slowly combines with sodium hydrogen sulphite to form *sodium triphenylmethylsulphonate*, $CPh_3{\cdot}SO_3Na,2H_2O$, which crystallises in large, lustrous plates. The free *acid* crystallises in sparingly soluble needles. When the carbinol is heated with aniline and acetic acid, the anilide, which has been previously prepared from aniline and triphenylbromomethane, is formed. Phenylhydrazine yields with the carbinol a substance which melts at 108·5° and is probably identical with the triphenylmethylazobenzene obtained by Gomberg from triphenylbromomethane. The carbinol also reacts readily with hydroxylamine, yielding a product, $C_{38}H_{32}O_2N$, melting at 182—184°, but the constitution of this substance has not been ascertained. Triphenylcarbinol readily combines with phenol, forming *hydroxytetraphenylmethane*, $CPh_3{\cdot}C_6H_4{\cdot}OH$, which crystallises in needles or plates and melts at 282°. This substance behaves as a phenol and yields a potassium salt which is readily soluble in alcohol. *Triphenyl*-p-*anisylmethane* is formed from the carbinol and anisole, and crystallises in needles melting at 194°. These reactions with sodium hydrogen sulphite, aniline, and phenol correspond with the reactions of nitrous acid with the same types of compounds, and the analogy is also supported by the ready esterification of the carbinol by alcohols, its union with sulphuric acid, and the formation of double salts of triphenylchloromethane and metallic chlorides.

The basicity of a number of methoxyl derivatives of benzylideneacetone and triphenylcarbinol was measured by ascertaining how much dilute alcohol was required to hydrolyse, and thus decolorise, solutions of molecular proportions of the various substances in a standard solution of acetic and sulphuric acids. Taking the basicity of dibenzylideneacetone as 1, those of the methoxyl derivatives are as follows: mono-*p*-compound, 3·9; *pp*-compound, 13·5; *oo*-compound, 3·7; *mm*-compound, 1·2. Similarly, taking the basicity of triphenylcarbinol as 1, we have mono-*p*-compound, 6·3; di-*p*-compound, 34; tri-*p*-compound, 286; tri-*o*-compound, 7·6; tri-*m*-compound, 1·7; *oop*-compound, 27·3. In both cases, the effect of the methoxyl group is greatest in the para-position, whilst a greater effect is produced by its introduction into triphenylcarbinol than into dibenzylideneacetone. Comparing the effect of the introduction of the group in the same position into successive rings, it is found that the basicity increases in geometrical ratio, and this leads to the important conclusion that the three phenyl groups of the carbinol have an equal influence on the basicity of the derivatives, so that it becomes improbable that the formation of coloured salts can be referred to the presence of a quinonoid group in which only one phenyl group is concerned.

The increased basicity produced by the introduction of the methoxyl groups is accompanied by an increase in the chemical activity of the hydroxyl group of triphenylcarbinol. Tri-*p*-anisylcarbinol is much more easily reduced than triphenylcarbinol, and also unites with sodium hydrogen sulphite much more rapidly, the reaction taking place at once, whilst in the case of the triphenyl-derivative it requires weeks for its completion. The *sodium* salt produced crystallises in large, colourless plates and has the formula

$$C(C_6H_4{\cdot}OMe)_3{\cdot}SO_3Na,\tfrac{1}{2}H_2O.$$

Tri-*p*-anisylcarbinol is at once acted on by hydrocyanic acid, forming *tri*-p-*anisylacetonitrile*, which crystallises in long, rectangular plates and melts at 128·5—129°. Triphenylacetonitrile has been prepared by heating triphenylchloromethane with mercuric cyanide. Tri-*p*-anisylcarbinol also reacts readily with aniline, forming a blue colouring matter.

These facts further confirm the conclusion that the activity of the hydroxyl group is conditioned, not by any one of the phenyl groups present in the molecule, but by the nature of the whole complex with which the hydroxyl is united.

The following new compounds have been prepared in the course of the work:

Benzylidene-p-*anisylideneacetone* (*p*-methoxydibenzylideneacetone) is obtained by the condensation of benzylideneacetone and *p*-anisaldehyde, and forms nodular crystals melting at 96·5°. Di-*o*-anisylideneacetone, prepared from acetone and *o*-methoxybenzaldehyde, crystallises in bright yellow, rhombic plates and has previously been obtained by Petrenko-Kritschenko. o-*Methoxybenzaldehyde* boils at 114—115° under 12 mm. pressure. *Di*-m-*anisylideneacetone* is prepared in a similar manner and purified by conversion into the hydriodide; it crystallises in yellow needles melting at 52—54°. The methoxydibenzylideneacetones behave towards acids in a similar manner to the parent substance.

Tri-o-anisylcarbinol is prepared by Grignard's method from iodoanisole and methyl *o*-anisate, and forms colourless, lustrous tablets melting at 181°. *Tri-m-anisylcarbinol* is prepared in a similar manner, and crystallises in tablets melting at 119·5°. *m*-Iodoanisole is prepared by converting *m*-nitroaniline into *m*-nitrophenol, methylating this with methyl sulphate, reducing, diazotising, and finally treating with hydriodic acid. The methyl *m*-anisate is prepared from *m*-hydroxybenzoic acid. oop-*Trianisylcarbinol* crystallises in large, lustrous prisms melting at 109—110°, and is prepared from *o*-iodoanisole and methyl *p*-anisate. *Diphenyl-p-anisylcarbinol*, prepared from bromobenzene and methyl *p*-anisate, forms crystalline crusts melting at 58—61°.

Tri-p-anisylchloromethane is formed when hydrogen chloride is passed into an ethereal solution of the carbinol, and is a white powder consisting of long prisms; it melts and decomposes at 154—156°, forming a red liquid which probably contains dimethylamine. A. H.

Auto-oxidation of Pyrogallol. By Carl D. Harries (*Ber.*, 1902, **35**, 2954—2959).—When pyrogallol dissolved in barium hydroxide solution is shaken with air, it undergoes oxidation, forming a *hexahydroxydiphenyl*, which probably has the constitution 3 : 4 : 5 : 3′ : 4′ : 5′. It crystallises from hot water in white needles which begin to decompose when heated to 200°, dissolves in alkali hydroxides giving deep coloured solutions, and reduces Fehling's solution, but yields no quinone when treated with an alcoholic solution of iodine. The *acetyl* derivative crystallises in small, colourless plates and melts at 162—163°.

Alkaline solutions of the substance absorb oxygen, but yield no trace of purpurogallin; it is therefore probable that for the formation of the latter by the auto-oxidation of pyrogallol (Berthelot, Abstr., 1898, i, 645) the presence of pyrogallol as well as the hexahydroxydiphenyl is necessary. R. H. P.

Halogen Derivatives of the Phloroglucinols. III. Decomposition of Tribromophloroglucinol. By Josef Herzig and Hermann Kaserer (*Monatsh.*, 1902, **23**, 573—581. Compare Abstr., 1886, 232; 1895, i, 343).—Tribromophloroglucinol is hydrolysed by aqueous potassium or barium hydroxide to carbon dioxide and a substance which forms a sparingly soluble barium salt apparently identical with the barium salt of dihydroxydiketo*cyclo*pentane described by Hantzsch (Abstr., 1888, 132). G. Y.

Halogen Derivatives of the Phloroglucinols. IV. Chloroderivatives of the Ethers of Phloroglucinol. By Hermann Kaserer (*Monatsh.*, 1902, **23**, 582—588. Compare preceding abstract).—When acted on by chlorine in carbon tetrachloride solution, phloroglucinol trimethyl ether forms trichlorophloroglucinol trimethyl ether, which melts at 130—131° and is identical with Bartolotti's compound (Abstr., 1897, i, 558). It can neither be acetylated nor reduced and is not acted on by boiling water or aqueous alkalis.

Phloroglucinol dimethyl ether yields, on chlorination, a *tetrachloro*-derivative, which crystallises from benzene in large, pale yellow, transparent crystals, melts at 115—117°, darkens on exposure to light, and is soluble in benzene, carbon tetrachloride, and concentrated sulphuric acid, but more sparingly so in light petroleum. It has an odour resembling that of camphor. It is decomposed by alkalis with formation of hypochlorites. The chlorine is only partly eliminated by the action of sodium amalgam or by boiling water. It cannot be acetylated. Reduction with stannous chloride and acetic acid leads to the formation of *trichlorophloroglucinol dimethyl ether*, which crystallises from benzene, melts at 93—95°, is soluble in aqueous alkalis, but is not changed by long boiling with alkalis, and forms an *acetyl* derivative crystallising in large, glistening flakes melting at 58—59° and easily soluble in benzene or light petroleum.

Chlorination of phloroglucinol methyl ether leads to the formation of a *pentachloro*-derivative, $OMe \cdot C_6Cl_5O_2$, which has a yellow colour, melts at 72—74°, is easily soluble in benzene and carbon tetrachloride, but sparingly so in cold light petroleum, and has scarcely any odour. Approximately 4 atoms of chlorine are eliminated by boiling with aqueous potassium hydroxide (compare Abstr., 1900, i, 595). G. Y.

Alkyl Ethers of the Phloroglucinols. V. Constitution of the Mono- and Di-alkyl Ethers of Methylphloroglucinol.

By Josef Herzig and Karl Eisenstein (*Monatsh.*, 1902, **23**, 563—572. Compare Abstr., 1901, i, 206).—The mono-methyl and mono-ethyl ethers of methylphloroglucinol, prepared by etherification with alcohol and hydrogen chloride, yield, on further etherification, two methyl-ethyl ethers, which are isomeric and must therefore be alkylated in the *op*-positions. This supports the contention of Bosse (Abstr., 1901, i, 207) that direct etherification of methylphloroglucinol takes place in the first instance in the *p*-position (compare Abstr., 1902, i, 463).

1-Methylphloroglucinol 4-ethyl ether crystallises from benzene in colourless, glistening needles, melts at 136—137°, boils at 195—200° under 13 mm. pressure, and is easily soluble in alcohol or ether. The *diacetyl* derivative crystallises from alcohol in colourless, soft leaflets and melts at 91°.

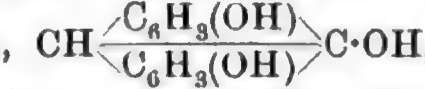
If, on etherification of the mono-alkyl ethers with alcohol and hydrogen chloride, the reaction be carried too far it results in a non-volatile product, but by stopping it before it has completely reached this stage, a mixture of the mono- and di-alkyl ethers is obtained by distillation. The di-alkyl ethers, which show little tendency to crystallise, are characterised by means of the dibromo- and acetyldibromo-derivatives.

Dibromomethylphloroglucinol ethyl ether $[Me : OEt : (OH)_2 : Br_2 = 1 : 4 : 2 : 6 : 3 : 5]$ crystallises from light petroleum and melts at 115°.

3 : 5-*Dibromomethylphloroglucinol* 4-*methyl ether* crystallises from

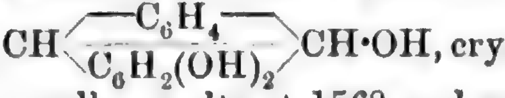
light petroleum in long needles, melts at 114°, and is easily soluble in alcohol or benzene.

3 : 5-*Dibromomethylphloroglucinol 2-methyl 4-ethyl ether* separates from dilute alcohol in colourless crystals, melts at 72—74°, and is easily soluble in alcohol, benzene, or light petroleum. The *acetyl* derivative crystallises from alcohol in long prisms and melts at 77—78°. 3 : 5-*Dibromomethylphloroglucinol 4-methyl 2-ethyl ether* is precipitated from glacial acetic acid, on addition of water, in colourless, hair-like needles and melts at 84—86°. The *acetyl* derivative forms monoclinic crystals from alcohol and melts at 99—101°. G. Y.

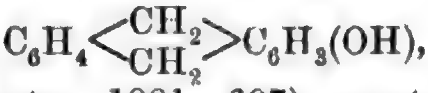
Reduction of Chrysazin with Hydrogen Iodide. By H. SCHROBSDORFF (*Ber.*, 1902, **35**, 2930—2931).—*Dihydroxyanthranol* (*chrysanthranol*),  $CH\left\langle\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}\right\rangle C\cdot OH$, crystallises from light petroleum in minute, lemon-yellow flakes or needles and melts at 176—177°. The *triacetyl* derivative crystallises in yellowish needles, melts at 209—210°, and is oxidised to diacetylchrysazin. T. M. L.

Reduction of Quinizarin and Anthrarufin with Hydrogen Iodide. By B. PLEUS (*Ber.*, 1902, **35**, 2923—2930).—In addition to quinizarin hydride, hydroquinizarol, and hydroxyhydroanthranol, which Liebermann and Giesel (Abstr., 1877, ii, 494) obtained as reduction products of quinizarin, 1 : 4-dihydroxyanthranol and hydro-α-anthrol have been obtained.

Triacetylhydroquinizarol, $CH_2\left\langle\begin{matrix}C_6H_4\\C_6H_2(OAc)_2\end{matrix}\right\rangle CH\cdot OAc$, prepared by heating hydroquinizarol with sodium acetate and acetic anhydride, forms yellow needles and melts at 79—80°; it is oxidised by chromic acid in acetic acid solution to diacetylquinizarin (Abstr., 1875, 68).

1 : 4-*Dihydroxyanthranol*,  $CH\left\langle\begin{matrix}C_6H_4\\C_6H_2(OH)_2\end{matrix}\right\rangle CH\cdot OH$, crystallises from alcohol in felted, orange-red needles, melts at 156°, and when dissolved in alkali and exposed to air becomes blue through conversion into quinizarin. The *triacetyl* derivative forms small, short, yellow prisms, melts at 188—189°, and is oxidised to diacetylquinizarin.

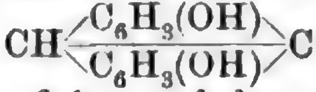
Diacetylhydroxyhydroanthranol, $CH_2\left\langle\begin{matrix}C_6H_4\\C_6H_3(OAc)\end{matrix}\right\rangle CH\cdot OAc$, crystallises in yellow needles and melts at 84—85°; this and the monoacetyl compound are oxidised by chromic acid to acetylerythro-oxyanthraquinone.

Hydro-α-anthrol,  $C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C_6H_3(OH)$, isomeric with Perger's hydroanthranol (Abstr., 1881, 607), crystallises in whitish-yellow flakes, melts at 94°, and is not very readily volatile in steam. The *acetyl* derivative forms yellow needles and melts at 82—85°.

Two new compounds were also obtained by reducing anthrarufin.

1 : 5-*Dihydroxyhydroanthranol*, $CH_2\left\langle\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}\right\rangle CH\cdot OH$, crystallises from dilute alcohol in golden-yellow needles and melts at 241°.

The *triacetyl* derivative crystallises in small, yellowish-white needles, melts at 162—163°, and is oxidised to diacetylanthrarufin.

1 : 5-*Dihydroxyanthranol*,  $CH{<}\begin{smallmatrix}C_6H_3(OH)\\C_6H_3(OH)\end{smallmatrix}{>}C{\cdot}OH$, crystallises from alcohol in glistening, golden flakes and decomposes at 200° without melting. The *triacetyl* derivative crystallises in stout, yellow, monoclinic prisms, melts at 184—185°, and is oxidised to diacetylanthrarufin; it is also formed when the dihydro-compound is dried at 120°, two atoms of hydrogen being eliminated.

Anthrarufin monoethyl ether, $OH{\cdot}C_{14}H_6O_2{\cdot}OEt$, crystallises from dilute alcohol in minute, short, canary-yellow needles and melts at 163—164°.

Acetylanthrarufin monoethyl ether, $OAc{\cdot}C_{14}H_6O_2{\cdot}OEt$, forms yellowish flakes and melts at 172—173°. The *diethyl* ether crystallises from alcohol in long, yellow, felted, silky needles and melts at 178°.

T. M. L.

Gradual Synthesis of the Benzene Chain. By MAURICE DELACRE (*Bull. Acad. roy. Belg.*, 1902, 251—258. Compare Abstr., 1900, i, 603).—The results now published extend and correct those recorded in a previous paper (*Bull. Acad. roy. Belg.*, 1895, 29, 849). When α-*iso*dypnopinacolin, $C_{32}H_{26}O$, is heated to 400° in a vacuum, it rapidly decomposes, furnishing (1) a liquid distillate containing ethylbenzene, allylbenzene, acetophenone, benzaldehyde, and benzoic acid; (2) a semi-solid fraction consisting of triphenylbenzene, *pyrodypnopinacolin*, and an uncrystallisable resin, which, on redistillation under atmospheric pressure, decomposes into ethylbenzene, polymerised allylbenzene, and triphenylbenzene (?).

Pyrodypnopinacolin, $C_{32}H_{22}O$, crystallises from alcohol in colourless crystals, melts at 166°, and distils between 465° and 475°. Its solubilities in the following media at their boiling points and at the ordinary temperature respectively are: acetic acid, 2·2 and 0·1; alcohol, 2·2 and 0·3; ethyl acetate and acetone, 10 and 1·3 per cent.; it is also more soluble in hot than in cold benzene. With acetic acid, ethyl acetate, benzene, acetone, and acetyl chloride, 2 mols. of the substance combine with 1 mol. of these solvents to form crystalline molecular compounds stable at 100—105°, but which decompose at 150—160°. The acetic acid additive product crystallises in colourless plates, melts at 162°, and is employed as a convenient means of separating pyrodypnopinacolin from the bye-products of its preparation. When reduced in alcoholic solution by means of sodium amalgam, or when treated with zinc ethyl, *pyrodypnopinacol alcohol*, $C_{32}H_{24}O$, is produced. The latter forms characteristically grouped, colourless needles, melts at 156° and distils at 310—328° under 15 mm., but when heated under atmospheric pressure (or in a vacuum if impure), it decomposes into benzaldehyde and a solid hydrocarbon, $C_{25}H_{18}$ (?). It dissolves in alcohol, acetic acid, or benzene, but is insoluble in light petroleum.

Pyrodypnopinalcolene, $C_{32}H_{22}$, is produced when pyrodypnopinacolin is treated with hydriodic acid (with concentrated acid, triphenylbenzene is also formed) or when pyrodypnopinacolyl alcohol is dissolved in acetyl chloride or acted on by phosphorus pentachloride. It crystallises in silky needles, which melt at 136°, or in large, transparent crystals, which melt at 154—156°, and boils at 330—333° under 15 mm. pressure. Its solubilities in the following media at their boiling points and at the ordinary temperature respectively are, alcohol, 1 and 0·11; acetic acid, 13·7 and 1·6; benzene, 153·8 and 35·6 per cent. When heated in alcoholic solution with sodium, or when oxidised by nitric acid, it is converted into *dehydropyrodypnopinacolyl alcohol*, $C_{32}H_{22}O$. This forms colourless crystals, melts at 203·5° and distils in a vacuum at 300—320° with slight decomposition. Its solubilities in the following media, at their boiling points and at the ordinary temperature respectively are: alcohol, 0·74 and 0·15; acetic acid, 4·16 and 1·13; benzene, 20·8 and 2·8 per cent. With the latter, an additive compound appears to be formed. When heated with hydriodic acid, pyrodypnopinalcolene is re-obtained. With acetyl chloride, *dehydropyrodypnopinacolyl acetate*, $C_{34}H_{24}O_2$, forming colourless crystals which melt at 200°, is produced. This dissolves readily in benzene, less so in acetic acid and alcohol. On saponification, the alcohol is not regenerated. When repeatedly recrystallised from acetic acid, it appears to be converted into the pyrodypnopinalcolene already described.

The author supposes that *a-iso*dypnopinacolin may be represented by the formula $C_8H_6OPh_4$, in which case pyrodypnopinacolin might be written $C_8H_2OPh_4$, or $C_8H_6OPh_2(C_6H_4)_2$, or $C_8H_4O(C_6H_4)_4$, the second or third expression being the more probable. T. A. H.

Aryl-sulphonated Alcohols and Acids. By JULIUS TROEGER and CHR. BUDDE (*J. pr. Chem.*, 1902, [ii], 66, 130—152. Compare Abstr., 1897, i, 223).—*Di-*m*-xylylethylenedisulphone*, $C_2H_4(SO_2{\cdot}C_8H_9)_2$, formed by the action of an alcoholic solution of ethylene dibromide on sodium *m*-xylenesulphinate, prepared by Gattermann's method from 1:3:4-xylidine, crystallises from alcohol in rosettes of needles, melts at 163°, is easily soluble in hot alcohol, more sparingly so in ether. When boiled with 30 per cent. potassium hydroxide solution, it yields *m*-xylenesulphinic acid and a semi-solid oil which is a mixture of m-*xylylsulphonethylic alcohol*, $C_8H_9{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, and its *ether*, $(C_8H_9{\cdot}SO_2{\cdot}C_2H_4)_2O$. The proportion of ether is increased if the hydrolysis be carried out under pressure. A preparation of di-*m*-xylylethylenedisulphone, obtained from a sulphinic acid prepared by reduction of *m*-xylenesulphonic chloride with zinc dust, melted at 146° and on hydrolysis yielded a xylenesulphinic acid melting at 55° and an oil consisting apparently of only xylylsulphonethylic alcohol. The following disulphones were obtained by prolonged warming of ethylene dibromide with the corresponding sodium sulphinate in alcoholic solution. *Di-*p*-xylylethylenedisulphone*, which crystallises from alcohol in needles, melts at 174° and on hydrolysis yields the sulphinic acid and p-*xylylsulphonethylic alcohol*, $C_8H_9{\cdot}SO_2{\cdot}C_2H_4{\cdot}OH$, as a light coloured oil. *Di-ψ-cumylethylenedisulphone*, $C_2H_4(SO_2{\cdot}C_9H_{11})_2$, which separates from alcohol in needles melting at 241° and, on hydrolysis with potassium hydroxide solution at 150°, yielding a mixture of *ψ-cumylsulphonethylic alcohol* and its *ether*, $(C_9H_{11}{\cdot}SO_2{\cdot}C_2H_4)_2O$. *Di-a-naphthylethylenedisulphone*, $C_2H_4(SO_2{\cdot}C_{10}H_7)_2$, which crystallises from alcohol in needles, melts at 194° and on hydrolysis yields *a-naphthylsulphonethylic alcohol*, $C_{10}H_7\cdot SO_2\cdot CH_2\cdot CH_2\cdot OH$, which is an oil. *Di-β-naphthylethylenedisulphone*, which crystallises from alcohol in needles, melts at 258° and yields *β-naphthylsulphonethylic alcohol* as a white, crystalline powder melting at 88—90°. *Di-*p*-chlorophenylethylenedisulphone*, $C_2H_4(SO_2\cdot C_6H_4Cl)_2$, crystallising from alcohol in microscopic needles which melt at 255° and on hydrolysis yielding the sulphinic acid and p-*chlorophenylsulphonethylic alcohol*, $C_6H_4Cl\cdot SO_2\cdot C_2H_4\cdot OH$, as a thick, brown oil. *Di-*p*-bromophenylethylenedisulphone*, which melts at 261° and yields p-*bromophenylsulphonethylic alcohol*, which forms a crystalline mass and melts at 50—52°. *Di-*o*-anisylethylenedisulphone*,

$$C_2H_4(SO_2\cdot C_6H_4\cdot OMe)_2,$$

which forms needles, melts at 175°, and yields o-*anisylsulphonethylic alcohol*, $OMe\cdot C_6H_4\cdot SO_2\cdot C_2H_4\cdot OH$, which forms a crystalline mass and melts at 82°. These arylsulphonethylic alcohols are easily soluble in alcohol or ether, more sparingly so in water.

The following arylsulphonacetic acids have been prepared by the action of ethyl chloroacetate on the corresponding sodium sulphinate and hydrolysis of the ester so obtained. m-*Xylylsulphonacetic acid*, $C_8H_9\cdot SO_2\cdot CH_2\cdot CO_2H$, is crystalline and melts at 56°. p-*Xylylsulphonacetic acid* is an oil. *ψ-Cumylsulphonacetic acid*, $C_9H_{11}\cdot SO_2\cdot CH_2\cdot CO_2H$, forms granular crystals and melts at 62°. *a-Naphthylsulphonacetic acid*, $C_{10}H_7\cdot SO_2\cdot CH_2\cdot CO_2H$, crystallises in glistening leaflets and melts at 168°. *β-Naphthylsulphonacetic acid*, $C_{12}H_{10}O_4S,H_2O$, forms a white, crystalline powder and melts at 90°; the *ethyl* ester,

$$C_{10}H_7\cdot SO_2\cdot CH_2\cdot CO_2Et,\tfrac{1}{2}H_2O,$$

melts at 82°, the *sodium* salt crystallises from alcohol in white needles. p-*Chlorophenylsulphonacetic acid*, $C_6H_4Cl\cdot SO_2\cdot CH_2\cdot CO_2H$, crystallises in small, glistening leaflets and melts at 122°, the *ethyl* ester is an oil. p-*Bromophenylsulphonacetic acid*, $C_6H_4Br\cdot SO_2\cdot CH_2\cdot CO_2H$, crystallises in needles and melts at 143°, the *ethyl* ester, $C_8H_6O_4SBrEt,H_2O$, crystallises in silky needles and melts at 52°. o-*Anisylsulphonacetic acid*, $OMe\cdot C_6H_4\cdot SO_2\cdot CH_2\cdot CO_2H$, crystallises in needles and melts at 138°, the *ethyl* ester is obtained as an oil which slowly solidifies.

The following alkylsulphones, $C_6H_3Me_2\cdot SO_2R$, have been obtained by the action of alkyl haloids on sodium *m*-xylenesulphinate. m-*Xylylmethylsulphone* forms crystals from alcohol and melts at 55°. m-*Xylylethylsulphone* solidifies on standing and melts at 53°. m-*Xylyl*-n-*propylsulphone* crystallises from dilute alcohol in needles and melts at 68—69°. m-*Xylyl*-*isopropyl-*, *butyl-*, *amyl-*, and *cetyl-sulphones* are oily substances and could not be obtained free from halogen. m-*Xylylallylsulphone* is obtained sometimes crystalline, sometimes as an oil; the compound last mentioned combines with bromine, forming a crystalline *dibromide* which melts at 56—57°.

o-*Anisylmethylsulphone*, $OMe\cdot C_6H_4\cdot SO_2Me$, crystallises from alcohol and melts at 84°. G. Y.

***p*-Hydroxytriphenylcarbinol. II.** By AUGUSTIN BISTRZYCKI and CARL HERBST (*Ber.*, 1902, **35**, 3133—3141. Compare Abstr., 1901, i, 701).—Crude, orange-coloured *p*-hydroxytriphenylcarbinol may be obtained perfectly colourless by repeated crystallisation from acetic acid and water, or by conversion into its acetyl derivative and subsequent hydrolysis with alkali and crystallisation from acetic acid. The *sodium* derivative, $ONa\cdot C_6H_4\cdot CPh_2\cdot OH$, forms colourless plates.

p-*Ethoxytriphenylcarbinyl ethyl ether*, $OEt\cdot C_6H_4\cdot CPh_2\cdot OEt$, crystallises from aqueous alcohol in colourless, microscopic plates melting at 87°. It may be obtained by the action of alkali and ethyl iodide or of hydrogen chloride and alcohol on the hydroxycarbinol. The *methyl* ether, $OMe\cdot C_6H_4\cdot CPh_2\cdot OMe$, melts at 74° and is readily soluble in most organic solvents with the exception of light petroleum. When boiled with glacial acetic acid, acetyl chloride, or acetic anhydride, the ethyl ether is converted into p-*ethoxytriphenylmethane*,

$$CHPh_2\cdot C_6H_4\cdot OEt,$$

which crystallises in well-formed, doubly refractive plates melting at 70—71°. The methyl ether, when similarly treated, yields p-*methoxytriphenylcarbinol* melting at 84°.

p-*Hydroxytriphenylmethane*, obtained by the reduction of the corresponding carbinol with zinc and acetic acid, crystallises in microscopic plates melting at 110°. The *methyl* ether melts at 61° and the *acetyl* derivative at 84°.

Dibromo-p-*ethoxytriphenylcarbinyl ethyl ether*,

$$OEt\cdot C_6H_2Br_2\cdot CPh_2\cdot OEt,$$

obtained by alkylating the dibromohydroxycarbinol (Abstr., 1901, i, 701), crystallises in well-formed plates melting at 105°. The *dimethyl* compound crystallises in microscopic prisms, melts at 98°, and when boiled with acetic anhydride yields an *ether*, $O(CPh_2\cdot C_6H_2Br_2\cdot OMe)_2$, melting at 133°. The diethyl compound under similar treatment yields *dibromo*-p-*ethoxytriphenylmethane* melting at 132°.

Dibromo-p-*hydroxytriphenylmethane*, obtained by the reduction of the carbinol, crystallises in small prisms melting at 131° and yields an *acetyl* derivative melting at 112—113°. Most of the ethers described do not give correct results for ethoxy- or methoxy-estimations by the Zeisel method.

J. J. S.

Constitution of a New *o*-Chlorodinitrobenzoic Acid and of *o*-Chloro-*m*-nitrobenzoic Acid. By ATTILIO PURGOTTI and A. CONTARDI (*Gazzetta*, 1902, **32**, i, 526—537).—The authors have determined the constitutions of the two following acids:

The dinitro-*o*-chlorobenzoic acid described by Kalle (D.R.-P. 106510) and melting at 199—200°. This acid is best prepared by heating at 130—140° a mixture of *o*-chlorobenzoic acid, sulphuric acid, and fuming nitric acid in suitable proportions. It boils at 240—241° and at 253° decomposes, and for the most part explodes; it is slightly soluble in water, but almost insoluble in the other solvents. Since when nitrated in the cold with a mixture of sulphuric and nitric acids, *o*-chlorobenzoic acid yields the nitro-*o*-chlorobenzoic acid melting at 165° described by Hübner (Abstr., 1884, 599), and this at higher temperatures gives, with the same nitrating mixture, Kalle's acid, the latter, as well as Hübner's acid, must have a nitro-group in the 3- or 5-position. Further, the dinitro-acid gives an almost theoretical yield of the methyl ester in presence of hydrogen chloride, and as position 2 is occupied by chlorine, position 6 must, according to

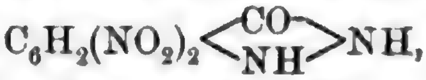
Victor Meyer's rule, be free. When heated with excess of ammonia solution, the acid yields the dinitroaminobenzoic acid, [$NH_2 : 2NO_2 = 2:3:5$], which, with dilute sodium hydroxide solution, gives the corresponding dinitrosalicylic acid, hence Kalle's acid has the constitution [$Cl : NO_2 : NO_2 = 2 : 3 : 5$]. When boiled with excess of barium hydroxide solution, it yields *o*-*p*-dinitrophenol. The acid may also be prepared synthetically by heating *m*-dinitrosalicylic acid with phosphorus pentachloride.

The *o*-chloro-*m*-nitrobenzoic acid described by Hübner (*loc. cit.*), when boiled for some time with excess of concentrated potassium hydroxide solution, yields the nitrosalicylic acid [$CO_2H : OH : NO_2 = 1 : 2 : 5$]. The constitution of the acid must hence be $CO_2H : Cl : NO_2 = 1 : 2 : 5$.

T. H. P.

Derivatives of *o*-Chlorodi-*m*-dinitrobenzoic Acid. II. By Attilio Purgotti and A. Contardi (*Gazzetta*, 1902, **32**, i, 573—579. Compare preceding abstract).—The following derivatives of *o*-chlorodi-*m*-dinitrobenzoic acid have been examined:

The *silver* salt, crystallising in thin, white needles; the *sodium* salt, forming yellow scales; the *potassium*, *ammonium*, *barium*, *calcium*, *copper*, *nickel*, *manganese*, cobalt, and lead salts were also prepared. The *methyl* ester forms small, acicular crystals which have a pungent odour, melt at 87°, and dissolve in methyl alcohol, and, to a less extent, in ether, water, or benzene. The *ethyl* ester forms plates melting at 54°, and is soluble in alcohol or ether. When heated with three molecular proportions of aniline, the acid reacts according to the equation $C_6H_2Cl(NO_2)_2 \cdot CO_2H + 3NH_2Ph = NHPh \cdot C_6H_2(NO_2)_2 \cdot CO_2H,NH_2Ph + NH_2Ph,HCl$. The *aniline o-phenylamino-di-*m*-nitrobenzoate* thus obtained crystallises from water in slender, shining, red needles which begin to decompose at 141° and at 253° melt and carbonise. The free *acid* forms orange-yellow needles which melt at 215° and are readily soluble in alcohol or benzene; the *potassium* salt forms bright red, shining leaflets.

The action of hydrazine hydrate on *o*-chlorodi-*m*-dinitrobenzoic acid yields an internal *anhydride* of the constitution  $C_6H_2(NO_2)_2 \Big< \substack{CO \\ NH} \Big> NH$, which separates from water in yellow prisms decomposing without melting at 185—215°.

T. H. P.

Methylanthranilic Acid. By Gustav Schultz and J. Flachsländer (*Chem. Centr.*, 1902, ii, 448; from *Zeit. Farb. Textilchem.*, 1902, 1, 353—354).—*Methylanthranilic acid*, $NHMe \cdot C_6H_4 \cdot CO_2H$, prepared by the action of methyl iodide on anthranilic acid, crystallises from alcohol in leaflets which show a greenish lustre, melts at 177°, and is soluble in alcohol or ether, forming solutions with a blue fluorescence; it is almost insoluble in water. When the acid is heated above its melting point, it decomposes, forming methylaniline, and when melted with alkali it yields indigo. The *hydrochloride*, $C_8H_9O_2N,HCl$, crystallises in needles, melts at 141°, and is readily soluble in alcohol, but only slightly so in water or ether. *Acetylmethylanthranilic acid*, $NAcMe \cdot C_6H_4 \cdot CO_2H$, crystallises in needles, melts at 192°, and is readily soluble in hot water or alcohol, but only sparingly so in ether *Methyl methylanthranilate*, $NHMe\cdot C_6H_4\cdot CO_2Me$, is liquid, has the odour of jasmine, and boils at 129° under 13 mm. pressure. *Nitrosomethylanthranilic acid*, $NO\cdot NMe\cdot C_6H_4\cdot CO_2H$, crystallises from benzene in reddish-yellow crystals, has not a definite melting point, and is readily soluble in alcohol, ether, or hot water. The *hydrochloride* of p-*nitrosomethylanthranilic acid*, $NHMe\cdot C_6H_3(NO)\cdot CO_2H,HCl$, dissolves in water or alcohol forming a green solution, and on heating forms *p*-nitrosomethylaniline with elimination of carbon dioxide. E. W. W.

Action of Formaldehyde on Anthranilic Acid. By GUSTAV HELLER and GEORG FIESSELMANN (*Annalen*, 1902, **324**, 118—137. Compare Abstr., 1901, i, 710).—*Methylenebisanthranilic acid*, $CH_2(NH\cdot C_6H_4\cdot CO_2H)_2$, prepared by adding 40 per cent. formaldehyde solution to an alcoholic solution of anthranilic acid, separates from acetone as a white, crystalline powder which becomes yellow at 150° and decomposes at 158°; it also crystallises from ethyl benzoate. It dissolves in alcohol but does not crystallise from this solvent, and it undergoes transformation when treated with glacial acetic acid. The ammoniacal solution of the compound yields precipitates with solutions of the salts of the heavy metals, but not with those of magnesium and the alkaline earth metals. The *diacetyl* derivative,

$$CH_2(NAc\cdot C_6H_4\cdot CO_2Na)\cdot NAc\cdot C_6H_4\cdot CO_2H,$$

produced by heating the preceding acid with acetic anhydride and anhydrous sodium acetate, is a colourless, crystalline powder decomposing at 284°; it is readily hydrolysed by dilute hydrochloric acid into formaldehyde and acetylanthranilic acid.

The methylene compound, when dissolved in pyridine and treated with benzoyl chloride, loses its methylene group and yields benzoylanthranil. Potassium cyanide decomposes the methylene compound into anthranilic acid and anthranilinoacetonitrile,

$$CN\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2H.$$

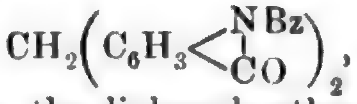
4 : 4′-*Diaminodiphenylmethane*-3 : 3′-*dicarboxylic acid*,

$$CH_2[C_6H_3(NH_2)\cdot CO_2H]_2,$$

obtained by heating the methylenebisanthranilic acid with dilute hydrochloric acid, is isolated in the form of its *hydrochloride*, $C_{15}H_{16}O_4N_2Cl_2$, by adding to the product excess of the concentrated reagent. The acid set free by the hydrolytic dissociation of its hydrochloride in aqueous solution crystallises in needles and decomposes at 254°. When heated with dilute hydrochloric acid at 200°, it readily loses carbon dioxide, yielding 4 : 4′-diaminodiphenylmethane. A solution of the neutral sodium salt of this acid yields a crystalline *calcium* salt, $C_{15}H_{12}O_4N_2Ca$, when treated with calcium chloride; similar insoluble salts are obtained by the interaction of solutions of other metallic salts.

The *ethyl* ester, $CH_2[C_6H_3(NH_2)\cdot CO_2Et]_2$, produced by heating the hydrochloride with ethyl alcohol and concentrated sulphuric acid, separates in aggregates of slender needles melting at 109°; the methyl ester, prepared in a similar manner, has already been described (Abstr., 1901, i, 470).

The *diacetyl* derivative, $CH_2[C_6H_3(NHAc)\cdot CO_2H]_2$, prepared by Pinnow's method, is insoluble in the ordinary organic solvents excepting glacial acetic acid, but dissolves in solutions of sodium acetate or alkali hydroxides and carbonates; it decomposes at 259—261°. The *dibenzoyl* derivative, produced by the Schotten-Baumann reaction, crystallises from glacial acetic acid in needles decomposing at 268°; it also dissolves in pyridine or in hot acetone or alcohol. This compound forms soluble alkali salts which are precipitated by excess of the alkali hydroxide or carbonate.

Dibenzoyldianthranilylmethane,  $CH_2\left(C_6H_3<\begin{matrix}NBz\\ |\\ CO\end{matrix}\right)_2$, resulting from the action of benzoyl chloride on the diphenylmethane derivative in pyridine solution, crystallises from this solvent in needles, or from toluene in sheaf-like aggregates, and melts at 287—288°; it is insoluble in dilute solutions of the alkali hydroxides, but when heated with excess of these reagents becomes converted into the alkali salt of the preceding benzoyl derivative.

The action of benzoyl chloride on anthranilic acid in pyridine solution also leads to the formation of the inner anhydride, which in this case is benzoylanthranil. G. T. M.

Substituted Aminobenzyl Cyanides and Iminobenzoyl Cyanides. By Franz Sachs and Max Goldmann (*Ber.*, 1902, **35**, 3319—3361).—A continuation of previous work (Abstr., 1899, i, 884, and 1901, i, 272). The general methods of preparing substituted aminobenzyl cyanides, CN·CHPh·NHR, and their oxidation products, the iminobenzoyl cyanides, CN·CPh:NR, are described in detail.

I. *Derivatives of Primary Monoamines.*—Anilinobenzyl cyanide (*loc. cit.*) yields a *nitroso*-derivative, CN·CHPh·NPh·NO, which crystallises in clusters of needles, melts at 55°, and when treated with benzaldehyde, benzotrichloride, and zinc chloride, forms derivatives of triphenylmethane. p-*Toluidinobenzyl cyanide* crystallises from light petroleum in prisms melting at 110°, and the *m*-compound in transparent leaflets melting at 97°. m-*Tolyliminobenzoyl cyanide* crystallises in yellow needles melting at 43°. α-*Naphthylaminobenzylcyanide* crystallises in leaflets melting at 113°, and the corresponding *iminobenzoyl cyanide* in lemon-coloured needles melting at 103°. β-*Naphthylaminobenzyl cyanide* crystallises in colourless clusters of laminæ melting at 119—120°, and the *iminobenzoyl cyanide* in small, yellow rods melting at 124°. p-*Bromoanilinobenzyl cyanide* crystallises in white leaflets melting at 99°, and the corresponding oxidation *product* in yellow, felted needles melting at 118°. *o*-Carboxyanilinobenzyl cyanide and the corresponding acid (this vol., i, 467) are completely destroyed by permanganate.

The *potassium* salt of *p*-sulphanilinobenzyl cyanide was obtained as a crystalline, white powder, and the *potassium* salt of *p*-sulphophenyliminobenzoyl cyanide as lustrous, long, pale yellow prisms. m-*Nitroanilinobenzyl cyanide* crystallises in fine, yellow needles melting at 109°, yields a *nitrosoamine* which crystallises in yellowish, compact prisms melting and decomposing at 90—91°, and, when hydrolysed, the corresponding *acid*, which crystallises in slender, yellow needles, melts at 151°, and forms a *nitrosoamine* melting at 156°; m-*nitrophenyliminobenzoyl cyanide* forms long, yellow, feathery, silky crystals melting at 120°. p-*Nitroanilinobenzyl cyanide* crystallises in bright yellow, rhombic laminæ melting at 128°, and the *azomethine* in long, lemon-coloured prisms melting at 128°.

II. Derivatives of Diamines and Aminophenols.—p-*Phenylenediaminodibenzyl cyanide*, $C_6H_4(NH\cdot CHPh\cdot CN)_2$, crystallises in microscopic prisms melting at 163°, and its oxidation product in orange-yellow prisms melting at 233°. The condensation *product* of acetyl-*p*-phenylenediamine and mandelonitrile crystallises in quadratic leaflets melting at 180°, and its oxidation *product* in orange-red needles melting at 146°. The corresponding *compounds* from benzoyl-*m*-phenylenediamine and mandelonitrile were also prepared; *phenyl-μ-cyanazomethine*-3-*benzoylaminophenyl*, $CN\cdot CPh\colon N\cdot C_6H_3\cdot NH\cdot COPh$, crystallises in yellow needles melting at 139°. The hydrolysis of *p*-dimethylaminophenylaminobenzyl cyanide yields the corresponding *amide*, which crystallises in straw-coloured needles, melts at 154—155°, is readily oxidised to the corresponding *azomethine* which crystallises in orange-yellow needles, and melts and decomposes at 170°, and when hydrolysed yields benzylidene-*p*-aminodimethylaniline. p-*Hydroxyanilinobenzyl cyanide* crystallises from alcohol in white leaflets, but is very unstable, as it readily evolves hydrogen cyanide and yields benzylideneaminophenol. p-*Ethoxyanilinobenzyl cyanide* crystallises in yellow, rhombic laminæ, melts at 85°, and when oxidised yields phenyl-*μ*-cyanazomethine-4-hydroxyphenyl.

Benzidine condenses with benzylidenecyanohydrin forming *bis-a-cyanobenzyl*-p-*diaminodiphenyl*, which crystallises in octahedra, melts at 201—202°, and when oxidised yields the corresponding *azomethine*, which crystallises in yellow needles and melts at 252°.

III. Derivatives of Aminoazo-compounds.—p-*Azophenyl-a-cyanobenzylaniline* crystallises in bronze-coloured needles, melts at 116°, and forms a *platinichloride*, which crystallises in large, red laminæ with a metallic lustre; the corresponding *azomethine* forms an orange-red, crystalline powder and melts at 138—139°. The analogous *compound* from benzeneazo-*β*-naphthylamine crystallises in red laminæ melting at 142°, and the *azomethine* in small needles which decompose at 198°.

Benzylidenecyanohydrin and benzeneazo-*a*-naphthylamine condense, forming a colourless *compound*, $C_{23}H_{17}N_3$, of undetermined constitution, which melts at 198° and is probably identical with the compound obtained by Goldschmidt and Rozell (Abstr., 1890, i, 614) by the condensation of benzaldehyde and benzeneazo-*a*-naphthylamine.

IV. Derivatives of Secondary Monoamines.—*Methylanilinobenzyl cyanide* crystallises in compact, white prisms melting at 67°, forms an unstable *nitrosoamine* which crystallises in yellowish-green plates decomposing at 80—83°, and a *mononitro*-derivative which melts at 127°.

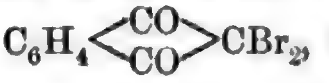
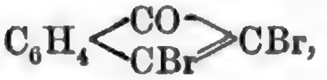
The *azomethine*, $NO_2\cdot C_6H_4\cdot C(CN)\colon N\cdot C_6H_4\cdot NMe\cdot CHPh\cdot CN$, is a dark red, crystalline powder which melts and decomposes at 174°. The *amide*, obtained by the hydrolysis of methylanilinobenzyl cyanide, crystallises in white needles melting at 133° and forms a more stable *nitroso*-derivative, which decomposes at 185—186°, a p-*nitro*-derivative, which melts and decomposes at 210°, and a *dinitro*-derivative, which decomposes at 170—172°. The *azomethine*,

$$NO_2\cdot C_6H_4\cdot C(CN)\colon N\cdot C_6H_4\cdot NMe\cdot CHPh\cdot CO\cdot NH_2,$$

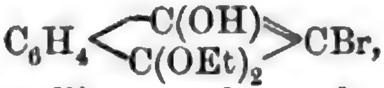
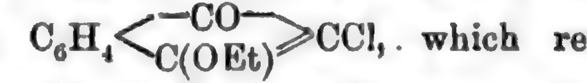
crystallises in small, dark purple pyramids, sinters at 182°, and decomposes at 200°.

Ethylanilinobenzyl cyanide is an oil which yields a crystalline *amide* melting at 135°. *Benzylaminobenzyl cyanide* crystallises in white needles melting at 134°. The triphenylmethane derivatives, nitrosoamines, and condensation products with nitrobenzyl cyanide of these two nitriles and their amides were also investigated. Attempts to obtain the corresponding acids from these amides were unsuccessful.

R. H. P.

Dibromocinnamic Acids and Dihalogen-indones. By A. Glawe (*Ber.*, 1902, **35**, 2936—2940).—By the action of concentrated sulphuric acid, β-dibromocinnamic acid is converted, after twenty hours, into dibromodiketohydrindene,  $C_6H_4{<}\substack{CO\\CO}{>}CBr_2$, the dibromoindone,  $C_6H_4{<}\substack{CO\\CBr}{>}CBr$, which is first formed being also converted into the same compound. a-Dibromocinnamic acid behaves in a similar manner, but only when heated to 110°. Dichloroindone does not behave in this way.

Bromodimethoxyhydrindone, $C_6H_4{<}\substack{C(OH)\\C(OMe)_2}{>}CBr$, prepared by the action of sodium methoxide on dibromoindone, crystallises from dilute methyl alcohol and melts at 79°. The corresponding *chloro*-compound melts at 85°.

Bromodiethoxyhydrindone,  $C_6H_4{<}\substack{C(OH)\\C(OEt)_2}{>}CBr$, separates from dilute alcohol as a white, crystalline powder and melts at 60—61°. *Chloroethoxyindone*,  $C_6H_4{<}\substack{CO\\C(OEt)}{>}CCl$, which results from the action of sodium ethoxide on dichloroindone, crystallises from alcohol in yellow needles and melts at 69—70°; chlorodiethoxyhydrindone appears also to be produced.

T. M. L.

Dinitrocinnamic Acid. By Paul Friedländer and R. Fritsch (*Monatsh.*, 1902, **23**, 534—542. Compare Abstr., 1885, 1137).—o-p-*Dinitrocinnamic acid*, prepared by Perkin's reaction from *op*-dinitrobenzaldehyde, crystallises from water or toluene in light yellow needles, melts at 179°, is easily soluble in hot water, benzene, alcohol, or glacial acetic acid, and dissolves on warming in sodium acetate solution. The *sodium, potassium, ammonium, barium, zinc, silver, lead, iron, manganese,* and *cobalt* salts are described; they all explode when heated. The *ethyl* ester crystallises from dilute alcohol in yellow needles, melts at 94°, is insoluble in water or light petroleum, and easily soluble in benzene or alcohol. The *dibromide*,

$$C_6H_3(NO_2)_2\cdot CHBr\cdot CHBr\cdot CO_2H,$$

formed by combination of bromine and *op*-dinitrocinnamic acid, crystallises from dilute alcohol in large, yellow needles, melts at 212°, is easily soluble in alcohol, ethyl acetate, or glacial acetic acid, is partially decomposed by hot water, and on addition of sodium hydroxide to the cold alcoholic solution immediately yields sodium bromide.

Reduction of *op*-dinitrocinnamic acid with ferrous sulphate and ammonia leads to the formation of a reddish-brown, amorphous precipitate. On reduction with stannous chloride and hydrochloric acid, aminocarbostyril is formed, which crystallises from dilute alcohol in long, colourless needles, becomes gradually red in colour, melts above 250°, is easily soluble in alcohol, glacial acetic acid, or hot water, less readily so in cold water, is dibasic, and forms crystalline salts.

op-Dinitrobenzylidenemalonic acid, $C_6H_3(NO_2)_2 \cdot CH:C(CO_2H)_2$, formed by the action of dinitrobenzaldehyde on malonic acid in presence of acetic acid, crystallises from water in colourless, delicate crystals containing $1H_2O$, melts at 49°; the anhydrous acid melts at 167°, but evolves carbon dioxide slowly at 150°. The *barium* and *silver* salts are described. The *diethyl* ester, formed from dinitrobenzaldehyde and diethyl malonate in presence of piperidine, crystallises from benzene in colourless needles and melts at 97°. G. Y.

Synthesis of Polycyclic Hydrocarbons.

By MAURICE DELACRE (*Bull. Soc. Chim.*, 1902, [iii], **27**, 875—882).—By the action of ethyl trichloroacetate on benzene in presence of aluminium chloride, the author has obtained fluorenecarboxylic acid, which is sparingly soluble in the ordinary solvents; the solutions are generally fluorescent. If slowly heated, the acid melts at 209—210°, but if it is first plunged into a bath heated to 180° it does not melt until 216—217°. It readily sublimes at 200° and undergoes decomposition at 280—290°, carbon dioxide being evolved and fluorene formed. The fluorene so obtained crystallises from alcohol in dazzlingly white, pearly scales, melts at 115°, and is quite unaltered by light. The acid obtained in this manner agrees in properties with that obtained by Friedländer (Abstr., 1877, 492), but the ethyl ester obtained from it is quite different, forming glassy crystals which melt at 60° and are very soluble in alcohol. The above synthesis appears to be a general one, and applicable to the formation of substituted fluorenes. A. F.

Affinities of the Halogenated Hydroxybenzoic Acids in Relation to their Constitution.

By ANGELO COPPADORO (*Gazzetta*, 1902, **32**, i, 537—572).—The author has measured the affinities of a large number of derivatives of benzoic acid containing at the same time one or more halogens and hydroxyl groups. The entry of a hydroxyl group into benzoic acid in either the ortho- or meta-position produces an increase in the affinity constant, whilst in the para-position a diminution takes place; when other hydroxyl groups now enter the molecule, they produce in some cases an increase, in others a decrease, in the affinity constant. Ostwald's method was used in the author's measurements, the temperature employed being 25°. The melting points of the acids examined are given in brackets.

5-Chlorosalicylic acid (172°) is 1·9 times as strong as salicylic acid; 3 : 5-dichlorosalicylic acid (219·5°), 2·4 times as strong as 5-chlorosalicylic acid; 5-chloro-2-ethoxybenzoic acid (118°), 1·6 times as strong as 2-methoxybenzoic acid; and 3 : 5-dichloro-2-methoxybenzoic acid (166·5°), 10 times as strong as 5-chloro-2-ethoxybenzoic acid.

2-Chloro-3-hydroxybenzoic acid (156—157°) and 6-chloro-3-hydroxybenzoic acid (178°) have equal affinity constants which are almost the same as that of 6-chloro-3-methoxybenzoic acid (168—169°); 2 : 6-dichloro-3-hydroxybenzoic acid (122—124°) has an affinity about 16 times as great as these. 2-Chloro-6-bromo-3-hydroxybenzoic acid (116—118°) has almost the same affinity as 2 : 6-dichloro-3-hydroxybenzoic acid, which confirms the constitution given by Martini (this vol., i, 150). Only about 1—1·5 per cent. of these acids are esterified by Fischer and Speier's method (Abstr., 1896, i, 201), whilst Martini's 6-chloro-2-bromo-3-hydroxybenzoic acid (194—195°) (*loc. cit.*) has an affinity 12 times as great as those of its two isomerides, and can be esterified to the extent of more than 70 per cent. by either V. Meyer's or Fischer and Speier's method; hence the bromine atom cannot be in the position 2, but must be at either 4 or 5.

3-Chloro-4-hydroxybenzoic acid (169—170°) has an affinity constant about double that of *p*-hydroxybenzoic acid; this is about the same change as is produced when a chlorine atom enters in the meta-position to the carboxyl in either benzoic or salicylic acid.

The two dichloroprotocatechuic acids, ($+3H_2O$, 220°) and (239°), show, when the dilution is great, almost equal affinities, and these are about the same as that of dichloroveratric acid (182—183°).

The methyl ($+1\frac{1}{4}H_2O$, 193°) and ethyl ($+2\frac{1}{2}H_2O$, 155°) esters of gallic acid have about equal dissociation constants, greater than that of pyrogallol. The affinity of the methyl ester of monochlorogallic acid ($+H_2O$, 159—160°) is about 2·6 times, and that of the ethyl ester ($+H_2O$, 106—107°) about twice, that of the corresponding gallic ester. The methyl ($+1\frac{1}{2}H_2O$, 160—170°) and ethyl ($+1\frac{1}{2}H_2O$, 151—153°) dichlorogallates have respectively 2·4 and 2·33 times the affinities of the above corresponding monochloro-compounds; methyl dibromogallate ($+1\frac{1}{2}H_2O$, 169°) gives still higher values for the affinity constant. The results obtained with ethyl dibromogallate ($+1\frac{1}{2}H_2O$, 137°) and methyl ($+1\frac{1}{2}H_2O$, 162—163°) and ethyl ($+1\frac{1}{2}H_2O$, 134—135°) chlorobromogallates were unsatisfactory.

T. H. P.

Reactions of Hydrocoumarone. By JOHANNES BOES (*Chem. Centr.*, 1902, ii, 370; from *Apoth.-Zeit.*, 17, 422).—Hydrocoumarone dissolves in concentrated sulphuric acid, forming a yellowish-red solution. The sulphonic acid and its salts are difficult to obtain in a crystalline form. *Hydrocoumaronesulphonic chloride* crystallises from alcohol in needles and melts at 81°. *Hydrocoumaronesulphonamide*, $C_8H_9O_3NS$, crystallises from alcohol and melts at 163°. Attempts to isolate an isomeric sulphonamide failed. Hydrocoumarone resembles hydrindene in its behaviour towards halogens, forming monohalogen hydrocoumarones, which have penetrating odours and do not boil under the ordinary pressure without decomposition. When sodium hydrocoumaronesulphonate is fused with potassium hydroxide, a hydroxy-compound is formed.

E. W. W.

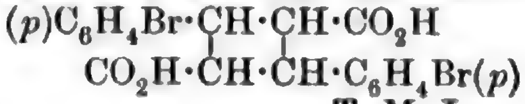
Anæsthetics. By Carl Goldschmidt (*Chem. Zeit.*, 1902, **26**, 743).—From *p*-phenetidine and its homologues and ethyl orthoformate, compounds of the type of methenyldi-*p*-phenetidine have been prepared which have an anæsthetic action. From *p*-aminobenzoic acid and ethyl orthoformate, by 10 minutes' boiling in alcoholic solution, a *compound*, $CO_2H\cdot C_6H_4\cdot NH\cdot CH{:}N\cdot C_6H_4\cdot CO_2H$, is obtained; it melts at 235°, and is soluble in alkalis and alkali carbonates; it acts both as an anæsthetic and an antiseptic. The analogous *compound* from *m*-aminobenzoic acid melts at 250°. From ethyl *p*-aminobenzoate and ethyl orthoformate the *compound*,

$$CO_2Me\cdot C_6H_4\cdot NH\cdot CH{:}N\cdot C_6H_4\cdot CO_2Me,$$

melting at 240°, and the *compound*, $CO_2Me\cdot C_6H_4\cdot NH\cdot CH(OEt)_2$, melting at 209°, are obtained. Methyl *p*-aminobenzoate reacts with formaldehyde in the presence of hydrogen chloride, yielding the *compound*, $CO_2Me\cdot C_6H_4\cdot NH\cdot CH_2Cl$, which, with alkalis, gives an amorphous base.
K. J. P. O.

Direct Conversion of Cinnamic Acid into α-Truxillic Acid. By C. N. Riiber (*Ber.*, 1902, **35**, 2908—2909).—Liebermann (Abstr., 1895, i, 470) showed that cinnamylidenemalonic acid was converted under the influence of light into an isomeric acid, which the author (this vol., i, 617) has proved to be a tetramethylene derivative; on oxidation, the latter yields α-truxillic acid. Since both cinnamic and α-truxillic acids are found in the leaves of *Erythroxylon coca*, it seemed possible that the action of light on the former gave rise to the formation of the latter acid. Very finely powdered cinnamic acid was exposed to light for three-and-a-half weeks, during which, however, there were only 50 hours of bright sunshine. Seventy per cent. of the acid was found to have been changed into α-truxillic acid, $C_{18}H_{16}O_4$, which crystallised in needles melting at 275°, and yielded a methyl ester (m. p. 173°). On distillation, cinnamic acid is re-formed.
K. J. P. O.

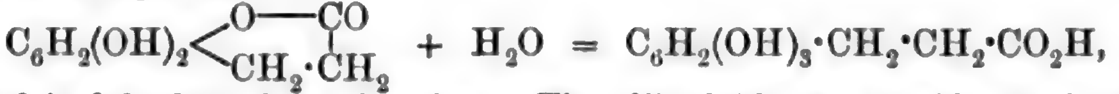
Dibromo-α-truxillic Acid. By R. Krauss (*Ber.*, 1902, **35**, 2931—2933).—*Ethyl dibromotruxillate*, $C_{22}H_{22}O_4Br_2$, crystallises from alcohol in colourless needles and melts at 124—126°. The *acid*, $C_{18}H_{14}O_4Br_2$, crystallises from acetic acid in small, colourless needles, melts at 260—264°, does not reduce permanganate, but when distilled is converted into bromocinnamic acid, which can then be oxidised to *p*-bromobenzoic acid. The constitution



$$\begin{array}{l} (p)C_6H_4Br\cdot \underset{|}{C}H\cdot \underset{|}{C}H\cdot CO_2H \\ \quad\quad\quad CO_2H\cdot CH\cdot CH\cdot C_6H_4Br(p) \end{array}$$

is therefore assigned to the acid.
T. M. L.

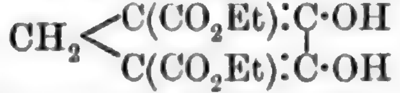
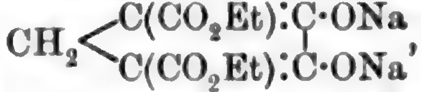
Dyes of the Æsculetin Series. II. By Carl Liebermann and S. Lindenbaum (*Ber.*, 1902, **35**, 2919—2923. Compare Abstr., 1901, i, 736).—When reduced in small quantities with sodium amalgam at 100° in a stream of carbon dioxide, æsculetin gives hydroæsculetin and *æsculetin dihydride*, $C_9H_8O_4$; the latter, which was separated by extracting the acidified solution with ether, crystallises from hot water in white flakes and melts at 198—200°; it is only slightly soluble in cold, but dissolves easily in hot, water, and partially remains in solution; similarly, when dissolved in ether, it separates as an oil and only becomes crystalline when heated; it is therefore probable that it adds on a mol. of water, perhaps with formation of a trihydroxyphenylpropionic acid,

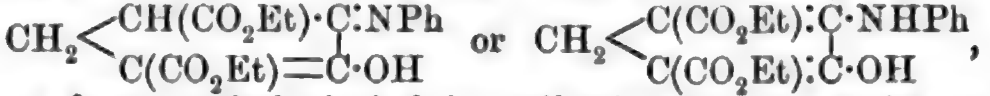


$$C_6H_2(OH)_2<\begin{array}{l}O—CO\\CH_2{\cdot}CH_2\end{array} + H_2O = C_6H_2(OH)_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

and is dehydrated on heating. The dihydride is not identical with Schiff's para-æsculetin (*Annalen*, 1872, 161, 84), and when treated with ammonia exhibits a striking series of colour reactions.

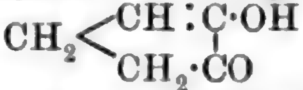
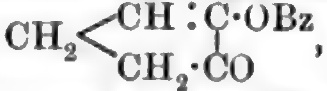
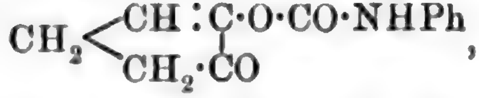
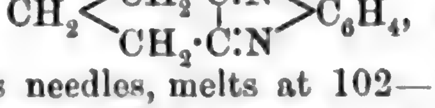
T. M. L.

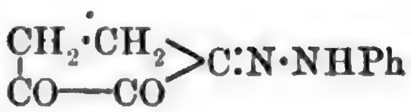
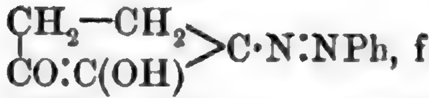
1 : 2-Diketopentamethylene (Δ^2-*cyclo*Pentene-1-one-2-ol) and Derivatives. By WILHELM DIECKMANN (*Ber.*, 1902, 35, 3201—3217).—Ethyl 1 : 2-diketopentamethylene-3 : 5-dicarboxylate (Abstr., 1894, i, 324),  $CH_2<\begin{array}{l}C(CO_2Et){:}C{\cdot}OH\\C(CO_2Et){:}C{\cdot}OH\end{array}$, has strongly acid properties; its aqueous alcoholic solution reddens blue litmus, it dissolves in dilute alkalis and alkali carbonates and also dissolves readily in sodium acetate solution; dry ammonia precipitates the ammonium salt as a colourless powder; it is stable towards alkalis and is not hydrolysed by concentrated hydrochloric acid; the *sodium* derivative,  $CH_2<\begin{array}{l}C(CO_2Et){:}C{\cdot}ONa\\C(CO_2Et){:}C{\cdot}ONa\end{array}$, is only slightly soluble in excess of alkali and is obtained either anhydrous or with $1\frac{1}{2}H_2O$; the *iron* salt forms a dark brownish-red, crystalline powder which dissolves sparingly with a violet coloration in ether. The *copper* derivative, $C_{11}H_{13}O_6Cu$, is a clear green, crystalline salt insoluble in all solvents and melts at 230°. The *osazone*, $C_{23}H_{16}O_4N_4$, crystallises from alcohol in minute, yellow needles and melts at 112°. The *phenazine*, $C_{17}H_{18}O_4N_2$, separates on warming an alcoholic solution of the ester with *o*-phenylenediamine in minute, yellow needles, crystallises from alcohol, and melts at 204°. The *monoanilide*,

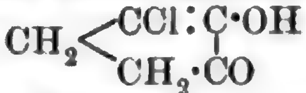
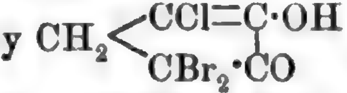
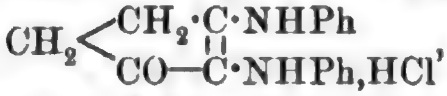


$$CH_2<\begin{array}{l}CH(CO_2Et){\cdot}C{:}NPh\\C(CO_2Et){=}C{\cdot}OH\end{array} \text{ or } CH_2<\begin{array}{l}C(CO_2Et){:}C{\cdot}NHPh\\C(CO_2Et){:}C{\cdot}OH\end{array},$$

separates from methyl alcohol in yellowish crystals, melts at 107°, dissolves in alkalis, and is precipitated unchanged by acids.

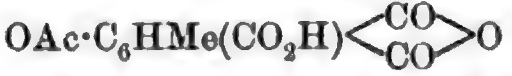
1 : 2-Diketopentamethylene,  $CH_2<\begin{array}{l}CH{:}C{\cdot}OH\\CH_2{\cdot}CO\end{array}$ (Abstr., 1897, i, 462), is best prepared by hydrolysing the ester with 20 per cent. sulphuric acid; it is oxidised by alkaline hydrogen peroxide to glutaric acid. The *benzoyl* derivative,  $CH_2<\begin{array}{l}CH{:}C{\cdot}OBz\\CH_2{\cdot}CO\end{array}$, separates from methyl alcohol in colourless crystals and melts at 72—73°. The *phenylurethane*,  $CH_2<\begin{array}{l}CH{:}C{\cdot}O{\cdot}CO{\cdot}NHPh\\CH_2{\cdot}CO\end{array}$, crystallises from benzene and melts at 122°. The *phenazine* derivative,  $CH_2<\begin{array}{l}CH_2{\cdot}C{:}N\\CH_2{\cdot}C{:}N\end{array}>C_6H_4$, separates from alcohol or water in colourless needles, melts at 102—103°, and distils without decomposition at about 290°; its solubility in water reaches a maximum at 70°.

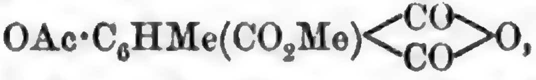
Phenylazo-1 : 2-*diketopentamethylene*,  $\begin{matrix}CH_2\cdot CH_2\\ CO—CO\end{matrix}>C:N\cdot NHPh$ or  $\begin{matrix}CH_2—CH_2\\ CO:C(OH)\end{matrix}>C\cdot N:NPh$, forms a red, crystalline precipitate, melts at 130°, and dissolves readily in alkalis and alkali carbonates.

3-*Chloro*-1 : 2-*diketopentamethylene*,  $CH_2<\begin{matrix}CCl:C\cdot OH\\ CH_2\cdot CO\end{matrix}$, is probably identical with the compound which Hantzsch (Abstr., 1889, 853) described as chloro-1 : 3-diketopentamethylene. *Chlorodibromo*-1 : 2-*diketopentamethylene*, probably  $CH_2<\begin{matrix}CCl=C\cdot OH\\ CBr_2\cdot CO\end{matrix}$, prepared by brominating the preceding compound, crystallises from carbon tetrachloride or water and melts at 121—122°. 3-*Anilino*-1 : 2-*diketopentamethylene*-2-*monoanil hydrochloride*,  $CH_2<\begin{matrix}CH_2\cdot C\cdot NHPh\\ CO—C\cdot NHPh,HCl\end{matrix}$, prepared by the action of aniline on a solution of the chloro-compound in acetic acid, forms yellow, crystal flakes, and becomes brown and decomposes and melts at 260°.

3-*Bromo*-1 : 2-*diketopentamethylene* melts at 155°. 3 : 5 : 5-*Tribromo*-1 : 2-*diketopentamethylene* forms colourless crystals and melts at 155°.

T. M. L.

Acetylation of Cochenillic Acid. By CARL LIEBERMANN and S. LINDENBAUM (*Ber.*, 1902, **35**, 2910—2919).—An *acetylcochenillic anhydride*,  $OAc\cdot C_6HMe(CO_2H)<\begin{matrix}CO\\ CO\end{matrix}>O$ [4 : 6 : 1 : 2 : 3 or 4 : 6 : 3 : 1 : 2], is obtained by acetylating cochenillic acid with a mixture of acetic anhydride and acetyl chloride; it crystallises from acetic acid in colourless plates and melts and decomposes at 152—153°. The *silver* salt, $C_{12}H_7O_7Ag$, forms minute, white needles, is somewhat soluble in water, and is readily decomposed. The *methyl* ether,

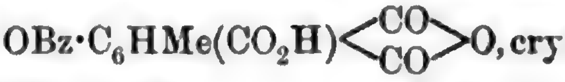


$$OAc\cdot C_6HMe(CO_2Me)<\begin{matrix}CO\\ CO\end{matrix}>O,$$

from the silver salt and methyl iodide, crystallises from ether in plates and melts at 136—138°.

Dimethyl acetylcochenillate, $OAc\cdot C_6H(CO_2Me)_2\cdot CO_2H$, prepared by boiling the preceding substance with methyl alcohol, crystallises from ether and melts at 149°.

By acetylating with acetyl chloride, only an *acetylcochenillic acetic anhydride*, $OAc\cdot C_6HMe(CO_2H)_2\cdot CO\cdot OAc$, was obtained in large, clear crystals which gradually became opaque; it softens and melts with decomposition at 230°. When exposed to air, it is hydrolysed into acetic acid and *acetylcochenillic acid*; the latter melts at 118—124°, resolidifies, and melts again with decomposition at 220°.

Trimethyl acetylcochenillate, $OAc\cdot C_6HMe(CO_2Me)_3$, prepared by heating the preceding compound with silver oxide and methyl iodide, crystallises from dilute acetic acid in needles and melts at 106—108°. It is hydrolysed by decinormal sodium hydroxide, giving *trimethyl cochenillate*, $OH\cdot C_6HMe(CO_2Me)_3$, which forms white needles, crystallises from water, melts at 136—138°, and gives a violet coloration with ferric chloride. By heating acetylcochenillic acid or its acetic anhydride at 70—80°, an *acetylcochenillic anhydride* is obtained isomeric with that described above; it melts at 140—148°, and on exposure to air is hydrolysed to acetylcochenillic acid; the latter, when heated at 115°, is converted, by the loss of a mol. of water, into *cochenillic anhydride*, $\mathrm{OH\cdot C_6HMe(CO_2H)}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{O}$, melting at 215—223° with decomposition. *Benzoylcochenillic anhydride*,  $\mathrm{OBz\cdot C_6HMe(CO_2H)}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{O}$, crystallises from benzene and melts at 187—189°. T. M. L.

Action of Light on Cinnamylidenemalonic Acid. By Elmer P. Kohler (*Amer. Chem. J.*, 1902, **28**, 233—240).

—An investigation of the white compound obtained by Liebermann (Abstr., 1895, i, 470) by the action of light on cinnamylidenemalonic acid has shown that it is a diphenyltetramethylenebismethylenemalonic acid,

$$\mathrm{C(CO_2H)_2{:}CH\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CHPh}}{\mathrm{CHPh}}>\mathrm{CH\cdot CH{:}C(CO_2H)_2},$$

a conclusion already arrived at by Riiber (this vol., i, 617). This acid readily combines with 2 mols. of hydrogen chloride; when its solution in methyl alcohol is saturated with hydrogen chloride, a *methyl* ester, $C_{28}H_{30}O_8Cl_2$, is produced which is soluble in hot acetone, crystallises in thick needles, and melts and decomposes at 197—198°; the corresponding *ethyl* ester, $C_{30}H_{34}O_8Cl_2$, melts and decomposes at 185°. When the acid is treated with bromine, an unstable additive compound is produced, which decomposes with elimination of carbon dioxide and hydrogen bromide and formation of *diphenyltetramethylenebisbromomethyleneacetic acid*, $\mathrm{CO_2H\cdot CH{:}CBr\cdot CH}<\genfrac{}{}{0pt}{}{\mathrm{CHPh}}{\mathrm{CHPh}}>\mathrm{CH\cdot CBr{:}CH\cdot CO_2H}$; the last-mentioned substance crystallises in colourless plates, melts and decomposes at 245°, is readily soluble in alcohol or acetone, and yields a-truxillic acid on oxidation with alkaline permanganate; its *methyl* ester melts at 115°. Diphenyltetramethylenebismethylenemalonic acid unites with 2 mols. of potassium hydrogen sulphite with formation of an additive *compound*. When the acid is dissolved in concentrated sulphuric acid and the solution is poured into water, cinnamylidenemalonic acid is precipitated. E. G.

Study of Lichens. X. By Wilhelm Zopf (*Annalen*, 1902, **324**, 39—78. Compare Abstr., 1899, i, 716).

—The name *protolichesteric acid* is given to a colourless, acidic substance obtained from *Cetraria cucullata*, this lichen yielding 2·2 per cent. of the compound, whilst *C. chlorophylla* furnishes only 0·5 per cent.; this acid can also be extracted from *C. complicata* and *C. islandica*, provided that ether is employed and not alcohol: the latter solvent causes the transformation of the subtance into its isomeride, lichesteric acid (m. p. 124—125°); this change is also effected by hot acetic anhydride. Protolichesteric acid, $C_{18}H_{32}O_5$, crystallises from benzene, light petroleum, ether, or alcohol in nacreous, rhombic leaflets melting at 103—104°. When separating slowly from dilute alcoholic solutions, it assumes the form of pyramidal, hemimorphous, rhombic crystals having an extinction parallel to the principal axis. The acid has a_D 12·1° at 19·5°, it dissolves in sodium hydrogen carbonate solution and in the presence of alkalis immediately decolorises potassium permanganate. Mineral acids reprecipitate the unchanged substance from its solutions in the alkali hydroxides, and although partly transformed into amorphous products, protolichesteric acid is not converted into lichesteric acid when heated above its melting point.

In *C. chlorophylla*, protolichesteric acid is accompanied by a small quantity of atranoric acid. *C. complicata* also furnished protocetraric, *l*-usnic, and atranoric acids. The lichesteric acid, isolated from *C. islandica* by Schnedermann and Knop, is in reality the product of the transformation of protolichesteric acid, and when ether or benzene is employed in the extraction only the latter substance is obtained.

The amorphous dilichesteric acid extracted from *C. islandica* var. *vulgaris* by Hesse is a decomposition product of protolichesteric acid formed by treating the latter substance with glacial acetic acid at 80°.

C. tubulosa (*C. juniperina* var. *tubulosa*) yields usnic, vulpic, and pinastric acids, the last being identical with the substance isolated from *C. pinastri*. In addition to these compounds, *C. tubulosa* furnishes a new substance, *cetrarialic acid* which separates in lustrous, pale olive-brown leaflets sparingly soluble in cold alcohol, ether, or benzene, but dissolving more readily on warming. In dilute potassium hydroxide solution, the new acid dissolves with evolution of gas; it is also soluble in an aqueous solution of sodium hydrogen carbonate.

Barbatic acid, isolated from *Usnea longissima* (Abstr., 1898, i, 99), forms a characteristic *sodium* salt which crystallises in rosettes of flattened, curvilinear needles. *U. cornuta* yields *d*-usnic and usnaric acids, the latter in larger quantity. *U. ceratina*, obtained from the pine trees of the Black Forest at an altitude of 700—800 metres, furnishes only barbatic acid and a trace of usnic acid ; this result is contrary to that of Hesse (Abstr., 1895, i, 298), the latter observer stating that barbatin and a large quantity of usnic acid are obtainable from the lichen. *U. dasypoga* accompanies the preceding species and yields barbatic, *d*-usnic, and usnaric acids, but not alectoric acid (compare Hesse, Abstr., 1900, i, 149). *Parmelia sinuosa* contains *d*-usnic acid and probably usnaric acid.

Thamnolic acid, a substance isolated from *Thamnolia vermicularis* when heated at 50—60° with concentrated hydrochloric acid, yields *thamnolin*, a reddish-brown, microcrystalline substance dissolving in hot water, alcohol, chloroform, or glacial acetic acid to a red solution. This product is also sparingly soluble in ether or benzene and develops a reddish-brown coloration with ammoniacal or alkaline solutions ; it is reprecipitated by hydrochloric acid, but not by carbon dioxide.

Cladina uncialis contains *d*-usnic and thamnolic acids, the former being identified by conversion into usnolic acid and the latter by the thamnolin reaction.

Squamatic acid, hitherto only obtained by Hesse from *Cladonia squamosa*, has also been isolated from *C. glauca*.

The presence of patellaric acid in *Urceolaria scruposa* has been confirmed ; it crystallises from 50 per cent. alcohol in flattened plates and decomposes at 165°. This acid gives a bluish-red coloration with bleaching powder and also develops an intense blue coloration with a solution of barium hydroxide or hydrated barium peroxide. Lecanoric acid has the same melting point and develops a similar coloration with bleaching powder, but not with barium hydroxide or peroxide. Olivetoric acid develops a bluish-green coloration with the latter of these reagents, but not with the former. Patellaric acid dissolves in sodium hydrogen carbonate and cold barium hydroxide solutions without decomposition and acids regenerate the unaltered substance; when heated with dilute potassium hydroxide solution, it develops a yellow coloration which then becomes red, and on adding a few drops of chloroform the liquid acquires a deep green fluorescence, which is rendered more distinct by cooling and diluting.

Lecanoric and atranoric acids could not be detected in the extracts from *U. scruposa*. G. T. M.

Reduction of Carboxylic Derivatives to Aldehydes and their Derivatives and to Amines. By FRANZ HENLE (*Ber.*, 1902, **35**, 3039—3044).—The hydrochlorides of the imino-ethers are readily reduced by sodium amalgam and dilute acids to the corresponding aldehydes. If the reduction be carried on in presence of phenylhydrazine or semicarbazide, the corresponding hydrazone or semicarbazone is obtained. Benzimino-ethyl ether hydrochloride is readily converted in this way into benzaldehyde, the yield amounting to 23·5 per cent. of the theoretical. In the presence of phenylhydrazine, the yield of benzylidenehydrazone is quantitative, and this reaction can readily be demonstrated, a voluminous precipitate of the hydrazone being formed. In the presence of semicarbazide, a yield of 52 per cent. of the theoretical amount of semicarbazone is obtained. In a similar manner, acetimino-ethyl ether hydrochloride yields 40 per cent. of the theoretical amount of ethylidenephenylhydrazone. In the absence of phenylhydrazine, the chief reaction is the hydrolysis of the imino-ether, but a certain amount of acetaldehyde is also produced.

Since phenylhydrazones can be reduced to amines, this reaction affords a new method of passing from the nitriles to the primary amines; all the operations being carried out at low temperatures.

Benzamidine hydrochloride is reduced by sodium amalgam and hydrochloric acid to benzylamine, the yield amounting to 38 per cent. of the theoretical. A. H.

***op*-Dinitrobenzaldehyde.** By PAUL FRIEDLÄNDER and PAUL COHN (*Monatsh.*, 1902, **23**, 543—562).—*op*-Dinitrobenzyl chloride is obtained in an almost quantitative yield when *p*-nitrobenzyl chloride is nitrated with a slight excess of nitric acid in concentrated sulphuric acid (compare Krassusky, *J. Russ. Phys. Chem. Soc.*, 1895, **27**, 335). It forms rhombic crystals, melts at 34°, is insoluble in water, sparingly soluble in light petroleum, but easily so in other ordinary solvents. It has little odour and is only slightly volatile with steam. op-*Dinitrobenzylaniline*, formed from *op*-dinitrobenzyl chloride and aniline in alcoholic solution, crystallises from benzene in orange-red crystals, melts at 132°, and forms a *hydrochloride* which crystallises in colourless needles or leaflets and is dissociated by water, and a *platinichloride* which is easily soluble in water. op-*Dinitrobenzyl*-p-*toluidine* crystallises from alcohol in delicate, red needles and melts at 93°. op-*Dinitrobenzyl-α-naphthylamine* crystallises from glacial acetic acid in dark red scales and melts at 164°. op-*Dinitrobenzylaniline*-p-*sulphonic acid* crystallises in yellow needles, is moderately soluble in water, and less readily so in alcohol; the *barium* and *silver* salts are described.

op-*Dinitrobenzyl acetate* crystallises in glistening, four-sided, thick plates, melts at 96—97°, is easily soluble in alcohol, benzene, or glacial acetic acid, but insoluble in light petroleum, and is hydrolysed by dilute sulphuric acid to op-*dinitrobenzyl alcohol*, which crystallises from alcohol in glistening, lemon-yellow needles, melts at 114—115°, and is easily soluble in alcohol, benzene, or glacial acetic acid, but insoluble in light petroleum. The action of nitric acid on *p*-nitrobenzyl alcohol dissolved in sulphuric acid leads to the formation of *p*-nitrobenzyl nitrate, and not of dinitrobenzyl alcohol. p-*Nitrobenzyl hydrogen sulphate* is formed when the alcohol is dissolved in concentrated sulphuric acid.

op-*Dinitrobenzaldehyde*, formed by oxidation of dinitrobenzylaniline-sulphonic acid with sodium dichromate in sulphuric acid solution, crystallises from a mixture of benzene and light petroleum in glistening plates, which become matt on exposure to light, melts at 68—69°, is easily soluble in most solvents, but sparingly so in water or light petroleum, and is only slightly volatile with steam. When warmed with sodium carbonate solution, the aldehyde is decomposed, with formation of a brown *substance*; with sodium hydrogen sulphite, it forms a crystalline *compound* easily soluble in water, and with phenylhydrazine in alcoholic solution it forms a *phenylhydrazone*, which crystallises in reddish-brown, hair-like needles, melts at 227—228°, and is sparingly soluble in the usual solvents. op-*Dinitrobenzylideneaniline*, formed from dinitrobenzaldehyde and aniline, crystallises from glacial acetic acid in thick, glistening, orange-yellow needles, melts at 131—132°, and is easily soluble in benzene or acetic acid, more sparingly so in alcohol. op-*Dinitrobenzylidene*-p-*toluidine* crystallises from glacial acetic acid in yellow needles and melts at 151°. op-*Dinitrobenzylidene-α-naphthylamine* crystallises in orange-red needles, melts at 202°, and is sparingly soluble in alcohol or glacial acetic acid. op-*Dinitrobenzaldoxime* crystallises from hot water in glistening, silky needles, melts at 127—128°, and is easily soluble in benzene, with a slight green colour, in the usual solvents, and in sodium hydroxide solution. The *benzoyl* derivative crystallises from glacial acetic acid in small, slightly yellow needles, sinters and melts at 165—166°. On prolonged boiling with acetic anhydride, the aldoxime is converted into *dinitrobenzonitrile*, which crystallises from alcohol in glistening, slightly brownish-yellow, rhombic plates, melts at 104–105°, and is easily soluble in ether, alcohol or benzene, but less readily so in carbon disulphide. op-*Dinitrobenzamide*, formed from the nitrile by the action of warm concentrated sulphuric acid, crystallises from water in long, glistening, slightly green needles, melts at 203—204°, and is converted by nitrous acid in 50 per cent. sulphuric acid solution into dinitrobenzoic acid, which is also formed when dinitrobenzaldehyde is boiled with silver acetate in acetic acid solution.

o-*Nitroso*-p-*nitrobenzoic acid* is formed from dinitrobenzaldehyde when its solution in benzene is exposed to direct sunlight. The nitroso-compound crystallises from ethyl acetate in glistening, slightly greenish-yellow leaflets, melts above 300°, and is sparingly soluble in the usual solvents, forming grass-green solutions when warmed. With aniline, it forms a yellowish-red *azo*-compound, and with methyl sulphate a *methyl* ester which crystallises from dilute acetic acid in glistening, yellow, silky needles, melts at 137—138°, and is more soluble than the acid. G. Y.

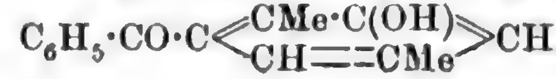
Condensation of Methyl Propyl Ketone with Benzaldehyde. By Carl D. Harries and P. Bromberger (*Ber.*, 1902, **35**, 3088—3090). —When these substances react in presence of dilute sodium hydroxide solution, *benzylidenemethyl propyl ketone*, $CHPh\colon CH\cdot COPr$, is formed as a yellowish oil which boils at 275° and has a sp. gr. 0·9979 at 17°; its *phenylhydrazone* melts at 99—100°, its *semicarbazone* at 150°, and its *oxime* at 97°. The oxime gives a *dibromo*-compound (m. p. 158°) when treated with bromine. On reduction, it yields the corresponding saturated ketone as a colourless oil which boils at 130° under 18 mm. pressure and has a sp. gr. 0·9614 at 17°.

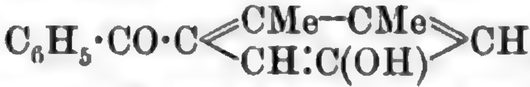
In presence of hydrochloric acid, the condensation takes place to *benzylidenepropyl methyl ketone*, $CH_2Me\cdot C(CHPh)\cdot COMe$, a yellow oil which distils at 120—130° under 18 mm. pressure and has a sp. gr. 1·0216 at 17°. Its *oxime* melts at 85°, its *phenylhydrazone* at 86°, and its *semicarbazone* at 207°. J. McC.

[Derivatives of] Hydroxybenzophenone. By Fritz Ullmann and Irma Goldberg (*Ber.*, 1902, **35**, 2811—2814. Compare Graebe and Ullmann, Abstr., 1896, i, 440).—o-*Hydroxyphenyl* p-*tolyl ketone*, $OH\cdot C_6H_4\cdot CO\cdot C_6H_4Me$, produced by condensing *o*-methoxybenzoyl chloride with toluene in the presence of aluminium chloride, separates from alcohol in large crystals, melting at 61·5°, and dissolving in sodium hydroxide solution to form a yellow sodium derivative; the *benzoyl* derivative melts at 80°; the *phenylhydrazone* and the *dibromo*-compound form yellow crystals melting at 145° and 132·5° respectively; the *oxime* is a white substance melting at 175°.

3-*Methoxybenzophenone*, $OMe\cdot C_6H_4\cdot COPh$, prepared from *m*-methoxybenzoyl chloride and benzene, boils at 342—343° under 730 mm. pressure, and solidifies to a crystalline mass melting at 37°; it is hydrolysed to 3-hydroxybenzophenone by hydrobromic acid.

4-Methoxybenzophenone, $OMe\cdot C_6H_4\cdot COPh$, obtained by employing *p*-methoxybenzoyl chloride in the preceding condensations, boils at 354—355° under 729 mm. pressure (compare Gattermann, Abstr., 1890, 962). G. T. M.

Synthesis of Two Benzoylxylenols. By Pietro Bartolotti and Adolfo Linari (*Gazzetta*, 1902, **32**, i, 494—503).—6-*Benzoyl*-1 : 4 : 2-*xylenol*,  $C_6H_5\cdot CO\cdot C\begin{matrix}\diagup CMe\cdot C(OH)\diagdown \\ \diagdown CH{=\!=}CMe\diagup\end{matrix}CH$, was prepared by first benzoylating 1 : 4 : 2-xylenol by Baumann's method, then heating the benzoyl compound with benzoyl chloride and zinc chloride, by which means benzoylxylenyl benzoate was obtained; the latter compound was then hydrolysed with aqueous alcoholic sodium hydroxide. Benzoyl-1 : 4 : 2-xylenol is deposited from alcohol in yellowish, shining scales melting at 166—167°; it is soluble in alkali hydroxides, giving a yellow coloration, but in dilute alcoholic solution it gives no coloration with ferric chloride. Its *acetyl* derivative, $C_{17}H_{16}O_3$, separates from aqueous alcohol in large, tabular, colourless crystals melting at 62—62·5°. The *methyl ether* is a dense, colourless liquid which boils at 194—195° under about 10 mm. pressure and is soluble in the ordinary solvents.

Benzoyl-1 : 2 : 4-*xylenol*,  $C_6H_5{\cdot}CO{\cdot}C{<}\begin{matrix}CMe{-}CMe\\CH{:}C(OH)\end{matrix}{>}CH$, prepared in a similar manner to its isomeride, separates from alcohol in yellow crystals which melt at 110—111° and are soluble in the ordinary solvents; it colours the alkali hydroxides yellow, and in aqueous alcoholic solution gives an intense black coloration with ferric chloride. Its *benzoyl* derivative, $C_{22}H_{18}O_3$, is deposited from alcohol in colourless crystals which melt at 110° and are soluble in the ordinary solvents. The *acetyl* compound, $C_{17}H_{16}O_3$, crystallises from dilute alcohol in shining, colourless scales melting at 74—74·5°. The *methyl ether*, $C_{16}H_{16}O_2$, separates from alcohol in colourless crystals melting at 82·5—83°.

T. H. P.

Hydroxy-derivatives of α-Naphthaquinone. By PAUL FRIEDLÄNDER and L. SILBERSTERN (*Monatsh.*, 1902, **23**, 513—533).—1 : 8-Aminonaphthol, formed by melting 1 : 8-aminonaphthalenesulphonic acid with sodium hydroxide (D.R.-P. 55404), crystallises from light petroleum in white needles, becomes grey on exposure to air, and melts and blackens at 94—97°. The *sulphate*, $(C_{10}H_9ON)_2,H_2SO_4$, separates from hot water in very slightly soluble crystals; the *hydrochloride* is sparingly soluble in concentrated hydrochloric acid and forms colourless crystals, which become grey on exposure to air. The *acetyl* derivative, $OH{\cdot}C_{10}H_6{\cdot}NHAc$, is soluble in aqueous alkalis, forms colourless crystals, and melts at 138°. With diazotised sulphanilic acid in acetic acid solution, aminonaphthol forms a red precipitate which, on reduction with zinc dust and dilute hydrochloric acid and treatment with ferric chloride, yields jugloe (8-hydroxy-α-naphthaquinone).

Naphthazarin (Will, Abstr., 1895, i, 668) is formed from 1 : 8-diaminonaphthalene, 1 : 8-dihydroxynaphthalene, or 1 : 8-aminonaphthol by condensation with 2 mols. of diazotised sulphanilic acid and reduction and oxidation of the product. With sodium hydroxide and 1 mol. of methyl sulphate, 2 : 3-dihydroxynaphthalene yields a mixture of the *mono-* and *di-methyl* ethers. The dimethyl ether is formed quantitatively by the action of 2 mols. of methyl sulphate. The monomethyl ether forms colourless needles, melts at 108°, has an odour resembling that of guaiacol, is easily soluble in the usual solvents, gives a green coloration with ferric chloride in alcoholic solution, and is volatile with steam. The dimethyl ether crystallises in colourless needles, melts at 115—116°, has an intense odour, and is slightly volatile with steam. The *monoethyl* ether melts at 109—110°, the *diethyl* ether at 96—97°.

Benzeneazodihydroxynaphthalene, formed from 2 : 3-dihydroxynaphthalene and 1 mol. of benzenediazonium chloride, crystallises from alcohol in glistening needles, and dissolves in alkalis to a yellowish-brown solution which becomes bright yellowish-red on addition of acid.

1-*Amino*-2 : 3-*dihydroxynaphthalene,* formed by addition of 1 mol. of diazotised sulphanilic acid to 2 : 3-dihydroxynaphthalene and reduction of the product with stannous chloride and hydrochloric acid, separates from hot water in small, white crystals, decomposes at about 230°, and is soluble in aqueous alkalis and in acids. Oxidation of the aminodihydroxynaphthalene by ferric chloride leads to the formation of a *quinone,* $C_{20}H_{10}O_7$ (?), which decomposes at about 250°, does not sublime, dissolves in alkalis with an intense bluish-violet colour, is reprecipitated unchanged by acids, and yields a tarry reduction product from which the quinone is re-formed by action of ferric chloride.

The action of 2 mols. of diazotised sulphanilic acid on 2 : 3-dihydroxynaphthalene leads to the formation of a dye which gives greyish-violet solutions in acids, reddish-violet in alkalis, and is reduced by stannous chloride and hydrochloric acid to 1 : 4-*diamino*-2 : 3-*dihydroxynaphthalene,* which is unstable when free, but forms a sulphate crystallising in glistening leaflets and yielding an intensely blue precipitate when warmed in aqueous solution in contact with air. Oxidation of the diamino-base with ferric chloride leads to the formation of *iso*naphthazarin.

Fusion of β-naphthol-3 : 6 : 8-trisulphonic acid (Abstr., 1883, 737) with sodium hydroxide leads to the formation of two dihydroxynaphthalenedisulphonic acids. The one which forms a sparingly soluble sodium salt crystallising in delicate needles, gives a rapidly fading blue coloration with ferric chloride, and reduces silver nitrate, must be 2 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, as in dilute solution it gives an intense bluish-violet coloration and forms a dark blue precipitate on addition of formaldehyde and concentrated hydrochloric acid. This reaction is found to be general for 2 : 8-dihydroxynaphthalenes. 2 : 3-Dihydroxynaphthalene-6 : 8-disulphonic acid forms a soluble sodium salt, and a sparingly soluble *barium* salt, but gives a stable violet coloration with ferric chloride, but yields no characteristic reaction with formaldehyde and concentrated hydrochloric acid.

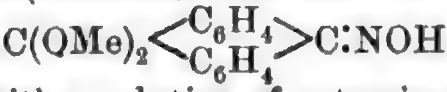
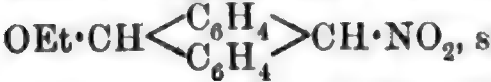
Prolonged fusion of the trisulphonic acid with sodium hydroxide results in the formation of 2 : 3 : 8-trihydroxynaphthalene-6-sulphonic acid; this reduces silver nitrate, gives with ferric chloride a green coloration, and with formaldehyde and concentrated hydrochloric acid a deep violet coloration and precipitate.

2 : 3 : 8-Trihydroxynaphthalene (D.R.-P. 112098), formed by heating the sulphonic acid with sulphuric acid at 180°, crystallises from xylene in yellow needles, melts at 175°, is easily soluble in water, alcohol, or ether, sparingly so in benzene or light petroleum, gives a dark blue coloration with ferric chloride in aqueous solution, and on warming with formaldehyde and hydrochloric acid forms a greyish-green precipitate. The *triacetyl* derivative forms green crystals, melts at 143—144°, and is easily soluble in benzene, glacial acetic acid, or alcohol, more sparingly so

in water, ether, or light petroleum. The *trimethyl ether*, prepared by the action of methyl sulphate and sodium hydroxide, crystallises from light petroleum in small prisms, melts at 127—128°, is insoluble in alkalis, and has, on warming, an odour resembling thymol.

When coupled with diazotised sulphanilic acid in dilute acetic acid solution, trihydroxynaphthalene forms an orange-red *dye* which, in solution, is changed to reddish-violet by sodium carbonate or ammonia, to bluish-violet by sodium hydroxide. On reduction of the dye with stannous chloride and hydrochloric acid, a *base* is obtained which forms a sparingly soluble, colourless, crystalline *sulphate* rapidly oxidised on exposure to air. Oxidation of the base with ferric chloride leads to the formation of a *quinone*, $C_{10}H_4(OH)_2O_2$, which crystallises from dilute alcohol in small, brownish-red, crossed needles, decomposes without melting at a high temperature, sublimes to a slight extent, gives with sodium carbonate a violet coloration, with sodium hydroxide a green coloration which disappears on warming, and forms a *diacetyl* derivative which crystallises from dilute acetic acid in golden-yellow leaflets, darkens at 55°, and melts at 65—67°. G. Y.

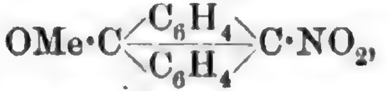
Anthraquinone. By K. DAMMANN and LUDWIG GATTERMANN (*Chem. Centr.*, 1902, ii, 368; from *Zeit. Farb. Textilchem.*, 1902, 1, 325—326).—The basic compounds formed by the action of dehydrating agents on α-arylaminoanthraquinones have been regarded as acridine derivatives. This view is confirmed by the fact that the acridine derivative prepared from *o*-acridylbenzoic acid is identical with the compound obtained by the action of phosphoric acid on α-anilinoanthraquinone. This *acridine* derivative, $C_{20}H_{11}ON$, prepared in the one case by boiling a solution of *o*-acridylbenzoic chloride in carbon disulphide with aluminium chloride, crystallises from a mixture of pyridine and methyl alcohol in orange-red leaflets and melts at 206°. E. W. W.

Reactions of Aromatic Nitro-compounds. By JAKOB MEISENHEIMER (*Annalen*, 1902, **323**, 205—246).—*Anthraquinoneoximedimethylacetal*,  $C(OMe)_2{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}C{:}NOH$, is prepared by heating nitroanthracene with a solution of potassium hydroxide in methyl alcohol, diluting the product with water, and precipitating the oxime with carbon dioxide; it crystallises from benzene or methyl alcohol in pale yellow needles, melts at 171°, and dissolves in the ordinary organic solvents but not in water; the *acetyl* derivative decomposes at 114°; the *methyl* ether separates in colourless crystals melting at 96°, the *benzyl* ether crystallises in yellow needles and melts at 69—70°. *Anthraquinoneoximediethylacetal*, obtained by the action of an alcoholic potassium hydroxide solution on nitroethoxydihydroanthracene,  $OEt{\cdot}CH{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}CH{\cdot}NO_2$, separates from benzene in granular crystals and decomposes at 172—173°. *Anthraquinoneoximemethylethylacetal* is produced either by treating anthracene ethyl nitrate with potassium hydroxide dissolved in methyl alcohol or by the action of an alcoholic solution of the alkali hydroxide on nitromethoxydihydroanthracene; it forms colourless crystals and decomposes at 134—135°.

Anthraquinonedimethylacetal, $C(OMe)_2<\substack{C_6H_4\\C_6H_4}>CO$, results from the oxidation of anthraquinoneoximedimethylacetal with an alkaline solution of potassium ferricyanide; it crystallises in transparent prisms, melts at 129°, and is readily soluble in the ordinary organic solvents. When treated in methyl alcohol solution with a trace of dilute sulphuric acid, the preceding acetal yields anthraquinone.

Anthraquinoneoxime results when the product of the action of methyl alcohol and potassium hydroxide on nitroanthracene is acidified with a mineral acid instead of carbon dioxide.

Nitromethoxydihydroanthracene, $OMe{\cdot}CH<\substack{C_6H_4\\C_6H_4}>CH{\cdot}NO_2$, which is readily prepared by adding concentrated nitric acid to anthracene suspended in benzene and methyl alcohol, yields an unstable *potassium* derivative crystallising in colourless, lustrous needles; this substance dissolves in water or methyl alcohol, but on prolonged heating with these solvents it decomposes, yielding nitroanthracene; it may also be crystallised from benzene. This derivative is also obtained by shaking together powdered nitroanthracene and a methyl alcohol solution of potassium hydroxide. When treated with potassium hypobromite, the potassium derivative yields bromonitromethoxydihydroanthracene, $OMe{\cdot}CH<\substack{C_6H_4\\C_6H_4}>CBr{\cdot}NO_2$, a substance separating from ether in well-defined, colourless crystals decomposing at 93°; this product, when boiled with methyl alcohol and potassium hydroxide, gives rise to nitromethoxyanthracene,



$$OMe{\cdot}C\substack{\diagup C_6H_4 \diagdown\\ \diagdown C_6H_4 \diagup}C{\cdot}NO_2,$$

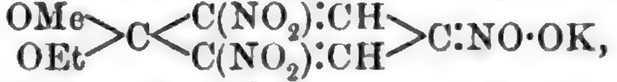
which crystallises in yellow needles and melts at 156°. This reaction also gives rise to a certain amount of nitroanthranol.

Bromonitroanthronedimethylacetal, $C(OMe)_2<\substack{C_6H_4\\C_6H_4}>CBr{\cdot}NO_2$, is produced by boiling nitromethoxyanthracene with a methyl alcohol solution of potassium hydroxide, diluting the liquid with water, and adding sodium hypobromite solution; it crystallises from methyl alcohol in white leaflets and decomposes at 139—140°. This acetal, unlike those previously described, is not affected by mineral acids.

Oxanthranyl methyl ether, $OMe{\cdot}CH<\substack{C_6H_4\\C_6H_4}>CO$, prepared by acidifying an ice-cold aqueous solution of the potassium derivative of nitromethoxydihydroanthracene with very dilute sulphuric acid, is separated from the nitroanthracene, also produced in this reaction, by successive crystallisation from chloroform and benzene; it crystallises from these solvents, or from the alcohols, in colourless prisms melting at 102·5°, and is probably identical with the substance described by Liebermann as melting at 98° (compare Abstr., 1889, 715).

iso*Nitromethoxydihydroanthracene*, $OMe{\cdot}CH<\substack{C_6H_4\\C_6H_4}>C{:}NO{\cdot}OH$, is obtained from the preceding experiment when the first chloroform extract is evaporated at 20—30° under diminished pressure instead of at 100°; on adding light petroleum to its chloroform solution, it separates in colourless, rhombic plates decomposing at 125°.

Potassium 3 : 5-dinitro-4-methoxy-4-ethoxyquinol-1-nitrolate,

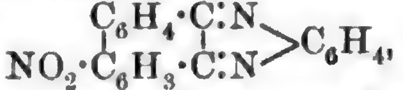


$$\begin{matrix}OMe\\OEt\end{matrix}>C<\begin{matrix}C(NO_2){:}CH\\C(NO_2){:}CH\end{matrix}>C{:}NO\cdot OK,$$

produced either by the action of potassium hydroxide on a solution of ethyl picrate in methyl alcohol or one of methyl picrate in ethyl alcohol, when decomposed by dilute sulphuric acid regenerates a mixture of the two alkyl picrates.

Potassium 3 : 5-*dinitro*-4-*ethoxy*-4-*isobutylquinolnitrolate*, produced by the action of potassium hydroxide on *iso*butyl picrate and ethyl alcohol or ethyl picrate and *iso*butyl alcohol, also yields a mixture of the two alkyl picrates on treatment with dilute sulphuric acid.

G. T. M.

Nitro-derivatives of Phenanthraquinone and of Phenanthraquinol. By Julius Schmidt and Adolf Kämpf (*Ber.*, 1902, **35**, 3117—3128).—3-Nitrophenanthraquinone is most readily prepared by the oxidation of 3-nitrophenanthrene (this vol., i, 29) with an acetic acid solution of chromic acid. It melts and decomposes at 279—280° (compare Schwabacher and Werner, this vol., i, 440) and may be crystallised from concentrated nitric acid. The nitro-derivative described by G. A. Schmidt as melting at 263° is undoubtedly impure (Abstr., 1879, i, 941). 3-*Nitrophenanthraquinonemono-oxime* crystallises from benzene in yellow needles melting at 240°. *Nitrodiphenylenequinoxaline*,  $\begin{matrix}C_6H_4\cdot C{:}N\\NO_2\cdot C_6H_3\cdot C{:}N\end{matrix}>C_6H_4$, obtained by the action of *o*-phenylenediamine hydrochloride on 3-nitrophenanthraquinone, crystallises in greenish-yellow needles melting at 252—253°. Anschutz's 10-bromonitrophenanthrene (*Ber.*, 1878, **11**, 1218) does not contain the nitro-group in position 3.

Hot fuming nitric acid converts phenanthraquinone into 2 : 7-dinitrophenanthraquinone melting at about 300° and an *isomeric* dinitro-derivative melting at 215—217°, and more readily soluble in acetic acid than the 2 : 7-dinitro-compound.

Phenanthraquinone and its nitro-derivatives are readily reduced to the corresponding quinols by the action of an alcoholic solution of phenylhydrazine acetate or of hydrogen sulphide. Phenanthraquinol, (9 : 10-dihydroxyphenanthrene) melts sharply at 147—148° after sintering at 130° and yields a *diacetyl* derivative melting at 202°. 3-*Nitro*-9 : 10-*dihydroxyphenanthrene* crystallises in rose-red needles with a bluish lustre, melts at 222—223°, and dissolves in alkalis to deep indigo-blue solutions which rapidly absorb atmospheric oxygen. Its *monoacetyl* derivative crystallises in yellow needles melting and decomposing at 234—235°.

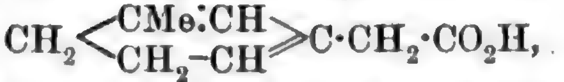
2 : 7-*Dinitro*-9 : 10-*dihydroxyphenanthrene* crystallises from alcohol in minute, brick-red needles melting and decomposing at 274°. It dissolves in sodium hydroxide, yielding a green solution which absorbs oxygen but slowly. The *monobenzoyl* derivative, $C_{24}H_{12}O_7N_2$, forms a yellow powder which sinters at 260° and is completely melted at 271°. The *diacetyl* derivative, $C_{18}H_{12}O_8N_2$, crystallises in pale yellow

needles melting and decomposing at 285°; on reduction, it yields a stable diamino-compound which, after diazotising, can be used for the preparation of sparingly soluble azo-dyes.

An isomeric *dinitro*-9 : 10-*dihydroxyphenanthrene* may be obtained by reducing the dinitrophenanthraquinone of unknown constitution with hydrogen sulphide; it crystallises in glistening, pale-red plates melting at 201°. Its *dibenzoyl* derivative melts at about 210° and its *diacetyl* derivative at 258°. J. J. S.

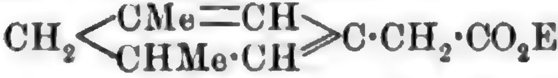
Enantiomorphic Structure of some Compounds of Camphor revealed by Etching. Resolution of Racemic Benzylidene Camphor. Isomorphism of its Active Components. By JULES MINGUIN (*Bull. Soc. Chim.*, 1902, [iii], **27**, 888—892).—The crystals of the camphor compounds have a completely symmetrical form, although in solution they are optically active. The author demonstrates, in the case of benzylidenecamphor and *p*-bromobenzylidenecamphor, that the corrosion figures obtained by means of benzene exhibit enantiomorphism. The author has also found that the enantiomorphic forms of benzylidenecamphor can give mixed crystals, so that the crystals of the one form can induce the crystallisation of the other. The author puts forward the idea that pseudo-racemism, and even true racemism, may be due entirely to the relative arrangement of the crystalline molecules of the oppositely active forms. A. F.

Terpenes and the Ethereal Oils. By OTTO WALLACH (*Annalen*, 1902, **323**, 135—160. Compare Abstr., 1901, i, 155—157).—[With HANS BÖTTICHER.]—$\Delta^{1:5}$-*Dihydro*-m-*tolylacetic acid*,

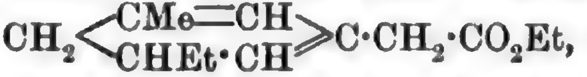


$$CH_2<\begin{matrix}CMe{:}CH\\CH_2{-}CH\end{matrix}>C\cdot CH_2\cdot CO_2H,$$

resulting from the hydrolysis of its ethyl ester with sodium methoxide, crystallises from alcohol in needles melting at 170—172°; the *amide* melts at 146—147°. The ester itself was not obtained pure, but is produced by condensing methyl*cyclo*hexenone with ethyl bromoacetate in the presence of zinc. The unsaturated acid yields dihydro-xylene when heated for 5 hours at 160°.

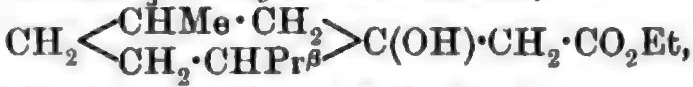
Ethyl $\Delta^{1:5}$-*dihydro*-3 : 5-*xylyl*-1-*acetate* (or 3 : 5-*dimethyl*-$\Delta^{1:5}$-*dihydrophenylacetate*),  $CH_2<\begin{matrix}CMe{=}CH\\CHMe\cdot CH\end{matrix}>C\cdot CH_2\cdot CO_2Et$, prepared by condensing 3 : 5-dimethyl*cyclo*hexenone with ethyl bromoacetate, boils at 136—137° under 18 mm. pressure; the *acid*, produced by hydrolysing the ester with sodium ethoxide and acidifying the product, crystallises from acetone or methyl alcohol in yellow flakes, melts at 150—152°, and boils at 170° under 15 mm. pressure; the *amide* melts at 126—127°. The two unsaturated acids are also characterised by their *silver* salts.

3 : 5-Dimethyl-$\Delta^{1:5}$-dihydrophenylacetic acid, when heated in closed tubes at 200°, yields $\Delta^{1:5}$-*dihydromesitylene*, which boils at 147° under the ordinary pressure and has a sp. gr. 0·826 at 18°. When the unsaturated acid is distilled with soda-lime, it yields a mixture of this hydrocarbon and mesitylene.

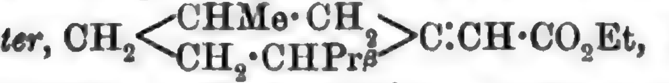
Ethyl propylidenebisacetoacetate, prepared by mixing propaldehyde with ethyl acetoacetate and slowly adding diethylamine to the mixture, crystallises from alcohol in silky needles melting at 76—78°; when heated with potassium hydroxide solution, it gives rise to *3-methyl-5-ethyl-*Δ^2-cyclo*hexenone*, a substance boiling at 102° under 14 mm. pressure and 232° under the ordinary pressure. This ketone, when condensed with ethyl bromoacetate, yields *ethyl 5-methyl-3-ethyl-*$\Delta^{1:5}$*-dihydrophenylacetate*,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CMe{=}CH}}{\mathrm{CHEt\cdot CH}}>\mathrm{C\cdot CH_2\cdot CO_2Et}$, from which the free unsaturated acid is obtained by hydrolysis with alkalis; the ester boils at 145—147° under diminished pressure, the acid melts at 141—143° and yields a *silver* salt and an *amide*, the latter melting at 123°. When heated in closed tubes at 200°, the acid yields a mixture of *s*-dimethylethylbenzene and a *hydrocarbon*, $C_{10}H_{16}$, boiling at 166—172° and having a sp. gr. 0·0834 at 20°; the latter substance is unsaturated, but does not furnish a solid nitrosochloride or nitrosite.

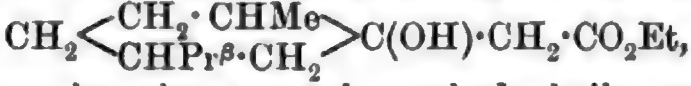
3-Methyl-5-*iso*propyl-Δ^2-*cyclo*hexenone is most conveniently condensed with ethyl bromoacetate by adding zinc turnings to the warm mixture diluted with benzene; the *ester*, $C_{14}H_{20}O_2$, thus produced boils at 154—158° under 16 mm. pressure and has the composition of an aromatic derivative; the corresponding *acid*, $C_{12}H_{16}O_2$, does not melt sharply, one portion fusing at 111—114° and another at 135—140°. The two fractions, however, have the same percentage composition. When heated at 200°, the acid yields a hydrocarbon boiling at 186—194° and having the properties of a *dimethyl*iso*propylbenzene*, $C_{11}H_{16}$.

[With Fritz Thölke.]—*Ethyl mentholacetate*,



$$\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CHMe\cdot CH_2}}{\mathrm{CH_2\cdot CHPr^{\beta}}}>\mathrm{C(OH)\cdot CH_2\cdot CO_2Et},$$

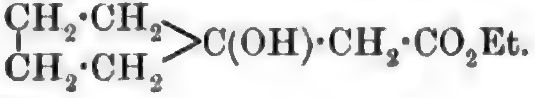
produced by condensing menthone with ethyl bromoacetate, boils at 150—152° under 14 mm. pressure and possesses an odour of cedar oil; the corresponding acid yields a well-defined *silver* salt. The *unsaturated ester*,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CHMe\cdot CH_2}}{\mathrm{CH_2\cdot CHPr^{\beta}}}>\mathrm{C{:}CH\cdot CO_2Et}$, results from the action of potassium hydrogen sulphate on the preceding ester at 140—150°; it boils at 140—142° under 14 mm. pressure; the *unsaturated acid* boils at 158—163° under 10 mm. pressure and is characterised by means of its *silver* salt. *Homomenthene*, $C_{11}H_{20}$, obtained by heating the unsaturated acid under pressure at 270—280°, boils at 186—187° under the ordinary pressure and has a sp. gr. 0·8215 and n_D 1·4579 at 23°. The hydrocarbon is probably 1:5-*dimethyl-2-ethyl-*Δ^1*-tetrahydrobenzene*.

Ethyl carvomentholacetate,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2\cdot CHMe}}{\mathrm{CHPr^{\beta}\cdot CH_2}}>\mathrm{C(OH)\cdot CH_2\cdot CO_2Et}$, produced from carvomenthone by the general method, boils at 162—164° under 16 mm. pressure and possesses the odour of cedar oil; the corresponding acid yields a *silver* salt, $C_{12}H_{21}O_3Ag$; the *unsaturated ester* boils at 150—152° under 13 mm. pressure, and the corresponding *acid* at 166—172° under 11 mm. pressure.

Homocarvomenthene, $C_{11}H_{20}$, obtained by heating the unsaturated acid, boils at 194—196° under the ordinary pressure and has a sp. gr. 0·8300 and n_D 1·46187 at 20°.

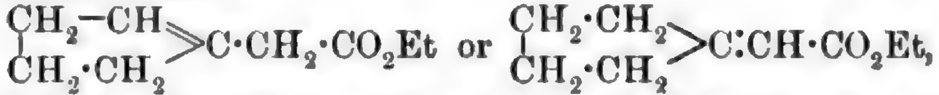
The condensation of carvenone with ethyl bromoacetate leads to the formation of an *unsaturated ester*, $C_{14}H_{22}O_2$, boiling at 135—137° under 16 mm. pressure: the *unsaturated acid* boils at 175—180° under 17 mm. pressure with slight decomposition; it yields a *silver* salt, $C_{12}H_{17}O_2Ag$. A *hydrocarbon*, $C_{11}H_{18}$, produced on heating the unsaturated acid at 250—260°, boils at 194—197° under the ordinary pressure and has a sp. gr. 0·851 and n_D 1·4821 at 22°. Homolimonene is analogous with the preceding compound and is obtained in the ordinary way from ethyl dihydrocarveolacetate (Abstr., 1901, i, 156); it boils at 191—192° and has a sp. gr. 0·8465 and n_D 1·4771 at 20°.

[With Nicolai Speranski.]—When condensed with ethyl bromoacetate, pentanone yields an oily product boiling at 105—107° under 11 mm. pressure which, although not obtained in a state of purity, is considered to be *ethyl* cyclo*pentanolacetate*,



$$\left.\begin{array}{l} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{array}\right> C(OH)\cdot CH_2\cdot CO_2Et.$$

The *unsaturated ester*,



$$\left.\begin{array}{l} CH_2-CH \\ | \\ CH_2\cdot CH_2 \end{array}\right\gg C\cdot CH_2\cdot CO_2Et \text{ or } \left.\begin{array}{l} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{array}\right> C{:}CH\cdot CO_2Et,$$

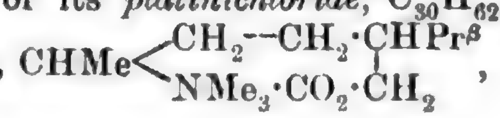
produced by heating the preceding compound with potassium hydrogen sulphate at 130°, is an oil boiling at 82—84° under 11 mm. pressure; the corresponding *acid*, $C_7H_{10}O_2$, boils at 122° under this pressure and melts at 49—50°; its *dibromide*, $C_7H_{10}O_2Br_2$, melts at 88° and its *amide*, $C_7H_9\cdot CO\cdot NH_2$, at 144°. On oxidation with chromic acid in glacial acetic acid solution, the preceding acid yields a small amount of pentanone.

G. T. M.

Terpenes and Ethereal Oils. Tetrahydrocarvone*iso*oxime. By Otto Wallach (*Annalen*, 1902, **323**, 323—333. Compare Abstr., 1900, i, 590).—[With L. Fresenius.]—Tetrahydrocarvone*iso*oxime (m. p. 104°), obtained by the transformation of tetrahydrocarvoneoxime, yields a crystalline hydrochloride, $C_{10}H_{19}NO,HCl$; this substance is, however, only produced in ethereal solution and is dissociated by water. The amino-acid (m. p. 201—202°), produced from the *iso*oxime by ring fission, is now shown to be *ε-amino-β-*iso*propylheptoic acid*, $NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$; its *ethyl* ester is a colourless, odourless liquid boiling at 149° under 20 mm. pressure; the *methyl* ester boils at 133—134° under 18 mm. pressure. When treated with sodium nitrite and acetic acid, the preceding ethyl ester gives rise to a mixture of *ethyl decenoate*, $CHMe{:}CH\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2Et$, and *ethyl ε-hydroxy-β-*iso*propylheptoate*,

$$OH\cdot CH_2Me\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2Et,$$

the former of these boiling at 108—111° and the latter at 152—155° under 13 mm. pressure.

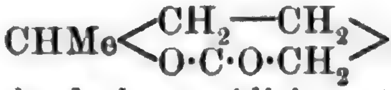
Ethyl ε-amino-β-*iso*propylheptoate combines with methyl iodide yielding the quaternary iodide, $C_{10}H_{18}O_2Et\cdot NMe_3I$; the substance, when treated with silver chloride, forms a hygroscopic chloride which is identified in the form of its *platinichloride*, $C_{30}H_{62}O_4N_2,H_2PtCl_6$. The corresponding betaine,  $CHMe\left<\begin{array}{l} CH_2-CH_2\cdot CHPr^{\beta} \\ \qquad\qquad\quad | \\ NMe_3\cdot CO_2\cdot CH_2 \end{array}\right.$, obtained by treating the quaternary iodide with silver oxide, is an amorphous, hygroscopic substance which yields a *platinichloride*,

$$(C_{10}H_{17}O_2NMe_3)_2,H_2PtCl_6.$$

The ε-amino-acid, when treated with nitrous acid, yields a mixture of three substances, a lactone, an unsaturated acid, and a hydroxy-acid. The first two only are volatile in steam. The non-volatile product is a viscid, non-crystallisable substance which yields a ketonic acid, probably *β-isopropyl-ε-ketoheptoic acid*,

$$CH_2Ac\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H\ ;$$

this compound melts at 37—38° and forms a semicarbazone melting at 151—152° (compare Baeyer and Villiger, Abstr., 1900, i, 133). On further oxidation, the hydroxy-acid gives rise to *iso*propylglutaric acid.

The lactone,  $CHMe{<}\substack{CH_2—CH_2\\ O\cdot C\cdot O\cdot CH_2}{>}CHPr^{\beta}$, is identical with the substance obtained by oxidising tetrahydrocarvone (Baeyer and Villiger, *loc. cit.*).

The unsaturated compound is a decenoic acid (Abstr., 1901, i, 590) having the formula $CHMe{:}CH\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$; the *amide* melts at 63—64° and on treatment with phosphoric oxide yields the nitrile, $C_9H_{17}CN$, a substance boiling at 99—100° under 12 mm. pressure. A base boiling at 89—90° under 12 mm. pressure is obtained by reducing the nitrile with sodium and alcohol; it yields an alcohol on treatment with nitrous acid. G. T. M.

Terpenes and Ethereal Oils. Compounds of the Thujone Series. By Otto Wallach (*Annalen*, 1902, **323**, 333—373. Compare Abstr., 1895, i, 619; 1897, i, 246).—*iso*Thujone, when oxidised with potassium permanganate solution, gives rise to a ketolactone and two acids.

The ketolactone, $C_{10}H_{16}O_3$, melts at 43—44° and yields a *semicarbazone*, $C_{10}H_{16}O_2{:}N\cdot NH\cdot CO\cdot NH_2$, melting at 188—189°.

The *oxime*, $C_{10}H_{16}O_2{:}NOH$, separates from dilute methyl alcohol in transparent, prismatic crystals melting at 155—156°; the *phenylhydrazone* forms snow-white crystals and melts at 144—146°.

The ketolactone is not identical with that obtained from thujamenthone.

The acidic products of the oxidation of *iso*thujone are ketonic acids having the formulæ $C_8H_{14}O_3$ and $C_9H_{16}O_3$, and are separated by the fractional crystallisation of their semicarbazones in alcohol.

The semicarbazone of the former acid melts at 188—189°; and acid regenerated from this derivative melts at 73—74°, boils at 145° under 10 mm. pressure, and when oxidised with sodium hypobromite decomposes into bromoform and *iso*propylsuccinic acid. This result indicates that the C_8 acid is an iso*propyllævulic acid* having one of the following formulæ, $CH_2Ac\cdot CHPr^{\beta}\cdot CO_2H$ or $CHAcPr^{\beta}\cdot CH_2\cdot CO_2H$.

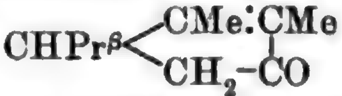
This acid yields an *oxime*, $C_8H_{14}O_2{:}NOH$, melting at 119—120° and a *phenylhydrazone* melting at 100—101°.

The other ketonic acid, $C_9H_{16}O_3$, is an odourless liquid boiling at 158° under 11 mm. pressure; its *semicarbazone* is readily soluble in hot alcohol and boils at 154—156°; the *oxime* melts at 77°. On oxidation with potassium hypobromite, the ketonic acid yields a lactone and a dibasic acid melting at 106—108° which is probably *iso*propylsuccinic acid.

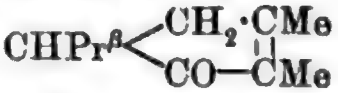
The ketolactone, when oxidised with permanganate, nitric acid, or sodium hypobromite, gives rise to an *acid*, $C_9H_{14}O_4$, which is isomeric with homoterpenylic acid and resembles this substance by crystallising with $1H_2O$; it crystallises from dilute methyl alcohol in plates melting at 52·5—53·5° and boils at 205—206° under 12 mm. pressure; its *silver* salt, $C_9H_{13}O_4Ag$, is soluble. When the oxidation is carried further by means of chromic acid, the preceding acid yields *iso*propyllævulic acid.

Benzylideneisothujone, $C_{10}H_{14}O{:}CHPh$, results from the interaction of benzaldehyde and *iso*thujone in the presence of an alcoholic solution of sodium ethoxide; it boils at 210—212° under 12 mm. pressure and melts at 83°.

Since *iso*thujone can be ultimately oxidised to an *iso*propyllævulic acid, its constitution must be represented either as

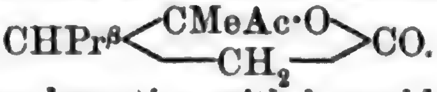
I. 

$$\mathrm{CHPr^{\beta}}\!<\!\begin{array}{l}\mathrm{CMe{:}CMe}\\ \quad\quad\quad\ \ |\\ \mathrm{CH_2{-}CO}\end{array}$$

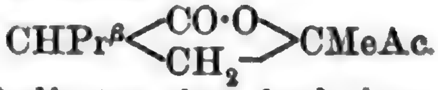
or II. 

$$\mathrm{CHPr^{\beta}}\!<\!\begin{array}{l}\mathrm{CH_2{\cdot}CMe}\\ \quad\quad\quad\ \ \|\\ \mathrm{CO{-}CMe}\end{array}$$

according as to whether the *iso*propyl group in the oxidation product is in an α- or a β-position. Assuming that Wagner's rule for the oxidation of ethylene derivatives holds in this case, the ketolactone must have one or other of the following formulæ,

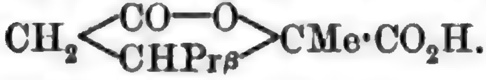
III. 

$$\mathrm{CHPr^{\beta}}\!<\!\begin{array}{c}\mathrm{CMeAc{\cdot}O}\\ \mathrm{CH_2}\end{array}\!>\!\mathrm{CO}$$

IV. 

$$\mathrm{CHPr^{\beta}}\!<\!\begin{array}{c}\mathrm{CO{\cdot}O}\\ \mathrm{CH_2}\end{array}\!>\!\mathrm{CMeAc}$$

The condensation with benzaldehyde indicates that *iso*thujone contains the residue $CO{\cdot}CH_2$, and accordingly formula I is to be preferred for the ketone. From this, the ketolactone should be represented by formula III, the acid $C_9H_{14}O_4$ being therefore represented by



$$\mathrm{CH_2}\!<\!\begin{array}{c}\mathrm{CO{-}O}\\ \mathrm{CHPr^{\beta}}\end{array}\!>\!\mathrm{CMe{\cdot}CO_2H}.$$

The constitution of the acid $C_9H_{16}O_3$ is still uncertain.

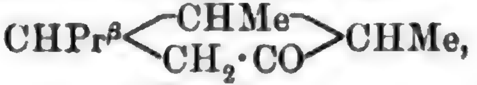
Thujamenthylamine, $C_{10}H_{19}{\cdot}NH_2$, the base obtained by reducing the oxime of thujamenthone, boils at 198—200° under the ordinary pressure and has a sp. gr. 0·8095 and n_D 1·4531. It yields *acetyl* and *benzoyl* derivatives and a *carbamide* and *phenylthiocarbamide*, these substances melting at 128—129°, 106—107°, 205—206° and 112° respectively; the *phenylcarbamide* is amorphous and the *hydrochloride* is crystalline.

Benzylidenethujamenthone, $C_{10}H_{16}O{:}CHPh$, produced by condensing *iso*thujone with benzaldehyde, boils at 180—182° under 11 mm. pressure but does not crystallise.

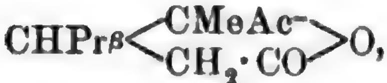
Thujamenthoketonic acid, $C_{10}H_{18}O_3$, the oxidation product of thujamenthone, yields a *silver* salt and a *semicarbazone*, $C_{11}H_{21}O_3N_3$, which melts somewhat indefinitely at 170—175° and is soluble in ammonia. The ketonic acid, on oxidation with sodium hypobromite, gives rise to a dibasic acid, $C_9H_{16}O_4$, which melts at 137—138° and crystallises from ether in transparent prisms; the *silver* salt has the composition $C_9H_{14}O_4Ag_2$.

The oxidation of thujamenthone also results in the formation of a ketolactone, $C_{10}H_{16}O_3$; this product crystallises from ether, melts at 42°, and boils at 130—132° under 10 mm. pressure; the *oxime* melts at

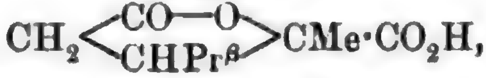
158—159°. The *semicarbazone* crystallises in needles and melts at 179—180°; the *phenylhydrazone* forms white leaflets melting at 144—146°. The ketolactone closely resembles the corresponding substance derived from *iso*thujone, and the two compounds yield semicarbazones, oximes, and phenylhydrazones which are very similar. The greatest difference is observed in their products of oxidation; the ketolactone from *iso*thujone gives a dibasic acid crystallising with $1H_2O$ and melting at 52—53°, whilst the ketolactone from thujamenthone yields an isomeric lactone-acid, $C_9H_{14}O_4$, which is anhydrous and melts at 94°; the product, on further oxidation, gives rise to *iso*propyllævulic acid. The following formulæ,



$$\mathrm{CHPr^{\beta}}<\begin{matrix}\mathrm{CHMe}\\ \mathrm{CH_2\cdot CO}\end{matrix}>\mathrm{CHMe},$$



$$\mathrm{CHPr^{\beta}}<\begin{matrix}\mathrm{CMeAc}\\ \mathrm{CH_2\cdot CO}\end{matrix}>\mathrm{O},$$

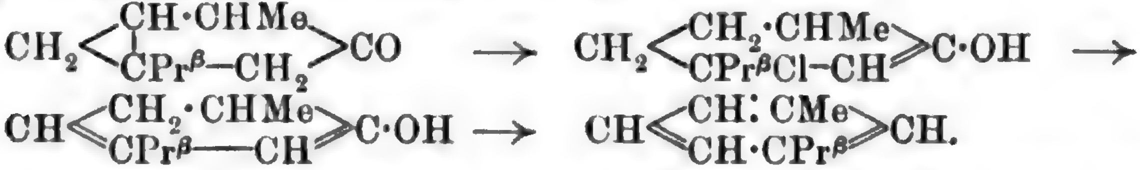


$$\mathrm{CH_2}<\begin{matrix}\mathrm{CO—O}\\ \mathrm{CHPr^{\beta}}\end{matrix}>\mathrm{CMe\cdot CO_2H},$$

are suggested for thujamenthone, the ketolactone, and the lactone-acid respectively.

Thujamenthoketonic acid and the dibasic acid (α-methyl-β-*iso*propylglutaric acid?) are regarded as having the constitutions $CHMeAc\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$ and $CO_2H\cdot CHMe\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$ respectively.

The formula for thujone suggested by Semmler (compare Abstr., 1893, 107; 1896, 330; 1897, i, 247) is confirmed by the observation that this ketone, when saturated with hydrogen chloride and heated at 120—150°, gives rise to a considerable quantity of cymene, the reaction being explained in the following manner:

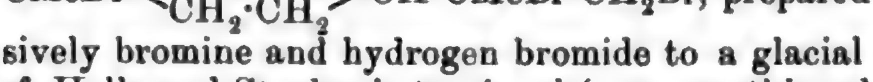


$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH\cdot CHMe}\\ \mathrm{CPr^{\beta}—CH_2}\end{matrix}>\mathrm{CO}\longrightarrow\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CHMe}\\ \mathrm{CPr^{\beta}Cl—CH}\end{matrix}>\mathrm{C\cdot OH}\longrightarrow$$
$$\mathrm{CH}\lessgtr\!\!<\begin{matrix}\mathrm{CH_2\cdot CHMe}\\ \mathrm{CPr^{\beta}——CH}\end{matrix}>\mathrm{C\cdot OH}\longrightarrow\mathrm{CH}<\begin{matrix}\mathrm{CH\colon CMe}\\ \mathrm{CH\cdot CPr^{\beta}}\end{matrix}>\mathrm{CH}.$$

The substance dihydrocarvacrol, represented by the third formula, is probably produced by the action of ferric chloride on thujone and under these conditions becomes oxidised to carvacrol.

The above formula for thujone does not, however, explain the formation of tanacetogenic acid and camphoric acid (m. p. 146°) from this ketone by the action of sodium hypobromite. G. T. M.

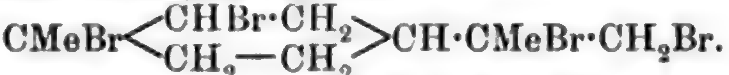
Terpenes and Ethereal Oils: Terpineol. By OTTO WALLACH and O. RAHN (*Annalen*, 1902, **324**, 79—97. Compare Abstr., 1895, i, 547; Tiemann and Semmler, *ibid*, i, 548).—1 :8 : 9-*Tribromoterpane*,



$$\mathrm{CMeBr}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMeBr\cdot CH_2Br},$$

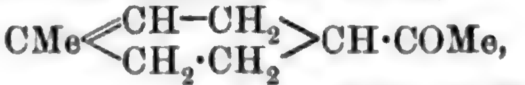
prepared by adding successively bromine and hydrogen bromide to a glacial acetic acid solution of Helle and Stephan's terpineol (compare this vol., i, 641), crystallises from dilute alcohol and melts at 67°. When treated with 1 mol. of bromine, the tribromide yields dipentene tetrabromide melting at 123°.

The *monobromide*, $C_{10}H_{15}Br$, produced by treating the tribromide with sodium methoxide in methyl alcohol solution, is an oily substance boiling at 105—110° under 10 mm. pressure, and yielding with bromine a *pentabromide*, which separates from alcohol or ethyl acetate in white crystals and melts at 137°. Assuming that the removal of bromine by sodium methoxide takes place in the same way as in the case of dipentene tetrabromide, the monobromide may be represented by the formula $\mathrm{CMe}<\begin{matrix}\mathrm{CH-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe{:}CHBr}$, whilst the pentabromide has a constitution corresponding with



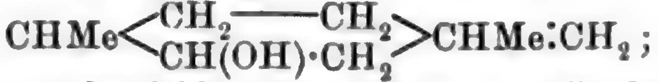
$$\mathrm{CMeBr}<\begin{matrix}\mathrm{CHBr\cdot CH_2}\\ \mathrm{CH_2-CH_2}\end{matrix}>\mathrm{CH\cdot CMeBr\cdot CH_2Br}.$$

Helle and Stephan's terpineol yields 1 : 8 : 9-trihydroxyterpane (m. p. 118°), and this in turn gives rise to the ketone $C_9H_{12}O_2$. When warmed with dilute sulphuric acid, the latter product loses water, and becomes converted into an unsaturated *ketone*,



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot COMe},$$

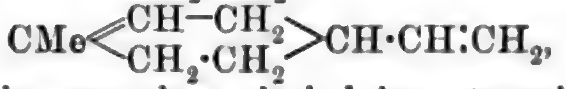
isomeric with phorone, which boils at 205—206° and has a sp. gr. 0·940 and n_D 1·4719 at 19°. The *semicarbazone* crystallises from alcohol in lustrous leaflets melting at 164—165°, the *oxime* melts at 51°, and on treatment with bromine yields the *dibromo-oxime* decomposing at 150°. The unsaturated ketone is a *p*-acetyltetrahydrotoluene, for when heated with concentrated sulphuric acid it loses hydrogen and furnishes *p*-acetyltoluene. The terpineol melting at 32° and dihydrocarveol are isomeric substances represented respectively by the formulæ $\mathrm{OH\cdot CMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe{:}CH_2}$ and



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2 \text{———} CH_2}\\ \mathrm{CH(OH)\cdot CH_2}\end{matrix}>\mathrm{CHMe{:}CH_2};$$

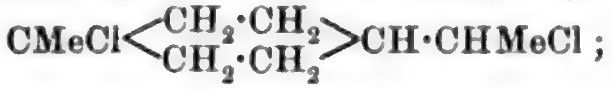
the latter compound yields successively a trihydroxyterpane, the hydroxyketone, $\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2 \text{———} CH_2}\\ \mathrm{CH(OH)\cdot CH_2}\end{matrix}>\mathrm{CH\cdot COMe}$, and the above-mentioned *p*-acetyltetrahydrotoluene; the final product, when reduced with sodium in dilute alcoholic or ethereal solution, gives rise to the terpineol, $\mathrm{CMe}<\begin{matrix}\mathrm{CH-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CHMe\cdot OH}$, which boils at 212—213°, and has a sp. gr. 0·942 and n_D 1·4836 at 19°; its *phenylurethane* crystallises from dilute methyl alcohol and melts at 69°. This alcohol, which is a lower homologue of the terpineol melting at 35°, when heated either with dilute solutions of oxalic or sulphuric acid or with sodium hydrogen sulphate at 180—190°, becomes converted into a lower homologue of cineol; this product boils at 168—172°, has a sp. gr. 0·92, and shows the characters of a saturated *oxide*, $C_9H_{16}O$, being stable towards potassium permanganate solution.

A *hydrocarbon*, $\mathrm{CMe}<\begin{matrix}\mathrm{CH-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C{:}CHMe}$ or



$$\mathrm{CMe}<\begin{matrix}\mathrm{CH-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CH{:}CH_2},$$

is obtained from the secondary alcohol by saturating its chloroform solution with hydrogen chloride and adding phosphorus pentachloride; it boils at 160—163°, and has a sp. gr. 0·843 and n_D 1·47586 at 22°. The action of hydrogen chloride and phosphorus pentachloride probably results in the formation of the saturated dichloride,



$$\mathrm{CMeCl}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CHMeCl};$$

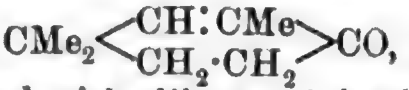
this product, by the loss of hydrogen chloride, would furnish a hydrocarbon having one or other of the formulæ just given. G. T. M.

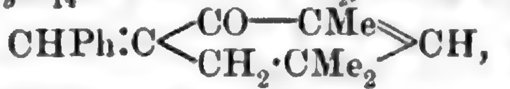
Terpenes and Ethereal Oils: Trimethyl*cyclo*hexenone, Trimethyl*cyclo*hexanone, and 3:3-Dimethyl*cyclo*pentanone. By Otto Wallach and A. Scheunert (*Annalen*, 1902, **324**, 97—112).—*a-cyclo*-Geraniolene, the chief product of the transformation of geraniolene, yields a nitrosochloride melting at 100—120° and a *nitrosate*, $C_9H_{16}O_4N_2$, melting at 102—104°. The corresponding *nitrolepiperidide*,

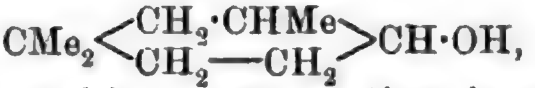
$$C_9H_{16}ON\cdot C_5NH_{10},$$

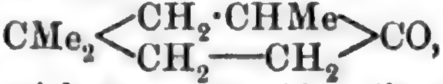
and *nitrolebenzylamine*, $C_9H_{16}ON\cdot NH\cdot CHPh$, melt respectively at 136—138° and 106°.

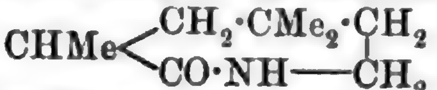
2 : 4 : 4-*Trimethyl*cyclo-Δ^2-*hexenoneoxime*, resulting from the action of alcoholic alkali hydroxides on the nitrosochloride or the nitrosate, boils at 131—132° under 15 mm. pressure and crystallises in prisms melting at 128—129°.

2 : 4 : 4-*Trimethyl*cyclo-Δ^2-*hexenone*,  $\mathrm{CMe_2}<\begin{matrix}\mathrm{CH{:}CMe}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CO}$, produced by hydrolysing the preceding compound with dilute sulphuric acid, is a colourless liquid boiling at 195—196° and having an odour resembling that of tanacetol; it has a sp. gr. 0·9245 and n_D 1·4749 at 25°; the molecular refraction, deduced from experiment, is 42·02, whilst the calculated value for an unsaturated alcohol containing two ethylene linkings is 42·16. Accordingly, the ketone appears to exist in the enolic form.

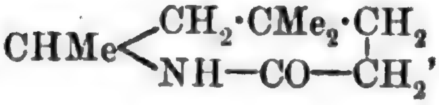
The *semicarbazone*, $C_9H_{14}N\cdot NH\cdot CO\cdot NH_2$, melts at 158—159°; the *benzylidene* derivative,  $\mathrm{CHPh{:}C}<\begin{matrix}\mathrm{CO{-\!-}CMe}\\ \mathrm{CH_2\cdot CMe_2}\end{matrix}>\mathrm{CH}$, obtained by condensing the ketone with benzaldehyde in the presence of sodium ethoxide, melts at 54—55°.

2 : 4 : 4-*Trimethyl*cyclo*hexanol*,  $\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CHMe}\\ \mathrm{CH_2{-\!-}CH_2}\end{matrix}>\mathrm{CH\cdot OH}$, results from the reduction of the unsaturated ketone with sodium in ethereal or alcoholic solution; in the former case, a considerable amount of pinacone is produced. The saturated alcohol is a viscid, colourless oil boiling at 192—193° and has a camphor-like odour.

2 : 4 : 4-*Trimethyl*cyclo*hexanone*,  $\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CHMe}\\ \mathrm{CH_2{-\!-}CH_2}\end{matrix}>\mathrm{CO}$, obtained by oxidising the preceding alcohol with chromic acid, boils at 191° and has a sp. gr. 0·902 and n_D 1·4545 at 19°; its *semicarbazone*, $C_9H_{16}N\cdot NH\cdot CO\cdot NH_2$, and *oxime* melt respectively at 164—165° and 108—109°. The latter derivative, when treated with moderately concentrated sulphuric acid, becomes transformed into the iso*oxime* melting at 115—116°; this product, when saturated with hydrogen chloride in ethereal solution, yields a stable *hydrochloride*. The iso*oxime* should have one or other of the formulæ



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CMe_2\cdot CH_2}\\ \mathrm{CO\cdot NH{-\!-}CH_2}\end{matrix}$$

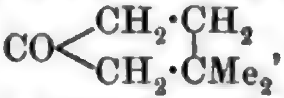
and  $\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CMe_2\cdot CH_2}\\ \mathrm{NH{-}CO{-}CH_2}\end{matrix}$, and, accordingly, the aminocarboxylic acid obtained by its hydrolysis with 20 per cent. hydrochloric acid at 150° is either *ε-amino-αγγ-trimethylhexanoic acid*,

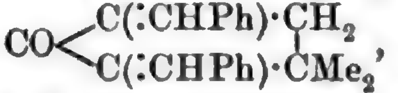
$$NH_2\cdot CH_2\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot CO_2H,$$

or *ε-amino-γγ-dimethylheptanoic acid*,

$$NH_2\cdot CHMe\cdot CH_2\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CO_2H.$$

This acid separates from dilute alcohol in colourless crystals melting at 160—161°.

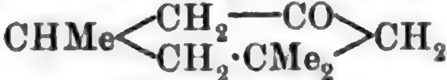
The constitution of 2 : 4 : 4-trimethyl*cyclo*hexanone is determined by studying the products of its oxidation. *iso*Geronic acid results from the action of potassium permanganate and is identified by means of its semicarbazone. The ketonic acid, on treatment with potassium hypobromite, yields *ββ-dimethyladipic acid*, which melts at 85—86° and is characterised by its *silver* salt and by conversion into 3 : 3-*dimethyl*cyclo*pentanone*,  $CO\left<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CMe_2\end{matrix}\right.$, through the agency of its calcium salt. This cyclic ketone, regenerated from its *semicarbazone* (m. p. 174—175°), boils at 154—155° and has the odour of menthone. The production of *dibenzylidene*-3 : 3-*dimethyl*cyclo*pentanone*,



$$CO\left<\begin{matrix}C(:CHPh)\cdot CH_2\\ C(:CHPh)\cdot CMe_2\end{matrix}\right.,$$

by the action of 2 mols. of benzaldehyde on the ketone in the presence of sodium ethoxide proves that the methyl groups are not in an α-position with respect to the carbonyl radicle.

The dibenzylidene derivative crystallises from ethyl acetate in brilliant, yellow needles and melts at 138—139°. *Benzylidene-ββ-dimethyl*cyclo*pentanone*, obtained from the ketone by the action of 1 mol. of benzaldehyde, is very soluble in alcohol or ether and separates from a mixture of the latter solvent and light petroleum in pale yellow crystals melting at 66—67°. G. T. M.

Terpenes and Ethereal Oils. Transformation of Cyclic Hydrocarbons and Ketones. By OTTO WALLACH and M. FRANKE (*Annalen*, 1902, **324**, 112—117. Compare preceding abstract).—Dihydro*iso*phorone, derived from *iso*phorone (compare Knoevenagel, Abstr., 1897, i, 611), has a constitution corresponding with the formula  $CHMe\left<\begin{matrix}CH_2—CO\\ CH_2\cdot CMe_2\end{matrix}\right>CH_2$, and is therefore 3 : 5 : 5-*trimethyl*cyclo*hexanone*, differing only from 2 : 4 : 4-*trimethyl*cyclo*hexanone*, produced from *cyclo*geraniolene, in the position of its carbonyl group. The first of these isomerides can be transformed into the second by the following series of changes.

The crystalline *trans*-dihydro*iso*phorol, $C_9H_{17}\cdot OH$, on treatment with phosphoric oxide or anhydrous zinc chloride, yields α-*cyclo*geraniolene, and this hydrocarbon, when treated in the manner indicated in the preceding abstract, gives 2 : 4 : 4-trimethyl*cyclo*hexanone.

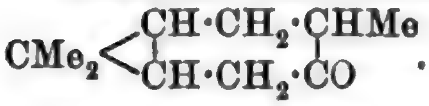
3-Methyl*cyclo*hexanol, when dehydrated with zinc chloride, gives rise to a *tetrahydrotoluene*, C_7H_{12}, which is isomeric with the hydrocarbon derived from methyl*cyclo*hexyl chloride. The new hydrocarbon yields a nitrosate, which, in turn, furnishes a methyl*cyclo*hexenone, $C_7H_{10}O$, differing in properties from 3-methyl*cyclo*hexanone (Knoevenagel, Abstr., 1897, i, 606). G. T. M.

Isomeric Changes in the Thujyl Series: Constitution of Thujone. By Iwan L. Kondakoff (*Chem. Zeit.*, 1902, **26**, 720—724).—Thujyl alcohol, which is probably a dicyclic compound, is converted by phosphorus pentachloride into an unstable thujyl chloride of inconstant composition (compare Semmler, Abstr., 1893, i, 178); it consists mainly of a tertiary compound which, with moist silver oxide, gives a tertiary alcohol, with bromine evolves hydrogen bromide, and with alcoholic potassium hydroxide forms a mixture of at least two hydrocarbons; these, in their properties, resemble, on the one hand, dicyclic thujene (Tschugaeff, Abstr., 1901, i, 38) and the sabinenes, and on the other, monocyclic tanacetene (Semmler, *loc. cit.*) and Wallach's thujene (Abstr., 1893, i, 105). From the hydrocarbon fraction (b. p. 160—175°), dipentene dihydrochloride can be obtained by treatment with hydrochloric acid. Thujyl chloride and hydrogen chloride yield two hydrochlorides, one of which is dipentene dihydrochloride. Thujone does not form an additive product with hydrogen chloride, but with hydrogen bromide gives a *substance* which boils at 105—117° under 11 mm. pressure; by moist silver oxide, it is converted into an optically inactive ketonic alcohol which boils at 229—231° under the ordinary pressure and at 105—106° under 11 mm. pressure, and has a sp. gr. 0·9314 at 20°, and n_D 1·4841; its *oxime* melts at 114·5—115°.

By prolonged treatment, or by warming, with hydrochloric acid, thujyl chloride is converted into a *dichloride* which boils at 116—130° under 12 mm. pressure, and is heavier than water; it is perhaps identical with the dichloride of dihydrocarveol.

Thujyl bromide is prepared by the action of hydrogen bromide on thujyl alcohol; it boils at 110—117° under 11 mm. pressure and has a sp. gr. 1·007 at 20° and $[\alpha]_D$ +23°5′; it appears to be a secondary compound.

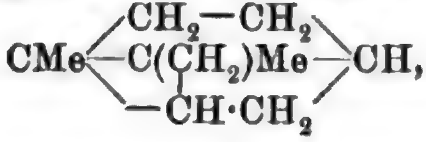
The author believes that thujone is best represented by the formula



$$CMe_2<\begin{matrix} CH\cdot CH_2\cdot CHMe \\ | \qquad\qquad | \\ CH\cdot CH_2\cdot CO \end{matrix}.$$

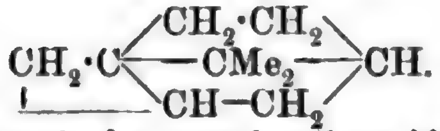
K. J. P. O.

The Constitution of Camphene. By Frank D. Dodge (*J. Amer. Chem. Soc.*, 1902, **24**, 649).—When pinene and camphene are treated with acetic acid containing 1 per cent. of sulphuric acid, they are converted to the extent of 43 and 77 per cent. into terpineol and *iso*bornyl acetates respectively, whilst limonene, terpinolene, and terpinene are, under the same conditions, esterified to the extent only of 4, 11, and 8 per cent. To account for this similarity in reaction of camphene and pinene, it is suggested that the former must contain, like the latter, a 3- or 4-carbon ring leading to one of the following formulæ for this hydrocarbon: 1.



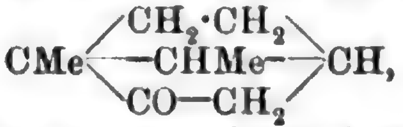
$$CMe\begin{matrix} CH_2-CH_2 \\ -C(CH_2)Me- \\ | \\ -CH\cdot CH_2 \end{matrix}CH,$$

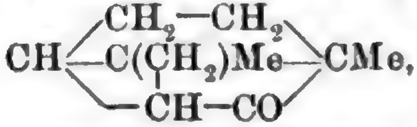
2.

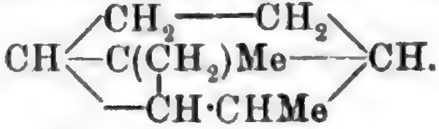


$$CH_2\cdot C\begin{matrix} CH_2\cdot CH_2 \\ -CMe_2- \\ CH-CH_2 \end{matrix}CH.$$

The second of these would lead to a formula for camphenilone identical with that proposed by Wallach for fenchocamphorone and is therefore improbable. The first formula represents camphene as a saturated substance which is in harmony with its behaviour to bromine and permanganate. It affords, further, an explanation of the formation of *iso*bornyl acetate by the opening of the 4-carbon ring; the position of the latter, however, precludes any further rearrangement of the rest of the molecule such as occurs in the corresponding reaction with pinene and so accounts for the possibility of reobtaining camphene from *iso*borneol. Whilst the new formula is in agreement with the constitution assigned to camphoric acid, camphenylic acid, and camphene glycol, it is not in harmony with Jagelki's formula for camphenilone (Abstr., 1900, i, 627). This, since it assumes the presence of an oxidised 4-carbon ring is improbable and it is proposed to substitute for it the following formula



representing camphenilone as a true lower homologue of camphor and satisfactorily accounting for its principal reactions. If the presence of a 4-carbon ring in camphene be admitted, the symmetry of the camphor molecule suggests the possible occurrence of such 4-carbon rings in other positions and the reactions of camphenone would be satisfactorily accounted for by the following formula: 

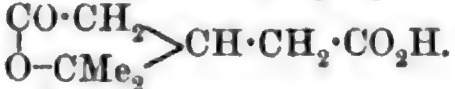
whilst fenchene, which reacts like pinene and camphene with acetic acid, would be represented thus: 

This formula, however, is not in harmony with Wallach's representation of fenchocamphorone (Abstr., 1900, i, 241).

T. A. H.

Oxidations with Mercuric Acetate. By Luigi Balbiano and Vincenzo Paolini (*Ber.*, 1902, **35**, 2994—2998; *Atti R. Accad. Lincei*, 1902, [v], **11**, ii, 65—69. Compare Abstr., 1902, ii, 109).—Mercuric acetate reacts with olefines at the ordinary temperature, insoluble mercurous acetate being formed, along with acetic acid and oxidation products of the olefine.

l-Pinene is thus converted into *dioxypinene*, $C_{10}H_{16}O_2$, which is a viscid oil of sp. gr. 1·069 at 0°, boils at 145° under 4 mm. and at 170—171° under 20 mm. pressure, and is optically inactive. This substance behaves as a ketonic alcohol containing an ethylene linking; it combines with two atomic proportions of bromine and yields an *oxime* melting at 138·5°, which also unites with bromine, and a *semicarbazone* which crystallises in needles melting at 180°. The *compound*, with phenylcarbimide, crystallises in prisms melting at 125°. Oxidation with permanganate converts it into terpenylic acid,



$$\begin{matrix} CO \cdot CH_2 \\ | \\ O-CMe_2 \end{matrix} > CH \cdot CH_2 \cdot CO_2H.$$

[With A. Nardacci.]—Anethole is converted by mercuric acetate into a *glycol*, $OMe \cdot C_6H_4 \cdot C_3H_5(OH)_2$, which crystallises in mammillary groups of needles and melts at 98°. The *diacetyl* derivative is an oil which boils at 210° under 41 mm. pressure. The glycol is oxidised by chromic acid to anisic acid.

[With E. LUZZI.]—*iso*Safrole, which contains the propenyl group, is readily oxidised by mercuric acetate, but the corresponding glycol has not yet been obtained pure. Safrole, on the other hand, which contains the allyl group, is not oxidised, but when treated with the acetate for four months yields a *compound*, $CH_2{:}O_2{:}C_6H_3{\cdot}C_3H_5(OH){\cdot}Hg{\cdot}OAc$, which forms crystalline crusts. An isomeric *compound* is obtained as a pale yellow syrup by the action of mercuric acetate for only 8—10 days. Both compounds, when treated with acids, yield safrole. Camphene behaves in a similar manner to safrole, yielding a crystalline mercury compound of complex constitution. A. H.

Essential Oil of Asarum Arifolium. By EMERSON R. MILLER (*Arch. Pharm.*, 1902, **240**, 371—385).—By distilling the roots of *Asarum arifolium* with steam, shaking the oil with aqueous potassium hydroxide, fractionating the residual oil, and examining the various fractions, the following constituents were detected: *l*-pinene, eugenol, a phenol of unknown composition, methyleugenol, methyl*iso*eugenol, safrole (the chief constituent), asarone, and probably a sesquiterpene.

C. F. B.

Constituents of Calamus Oil. I. By HERMANN THOMS and R. BECKSTROEM (*Ber.*, 1902, **35**, 3187—3195. Compare Abstr., 1901, i, 396).—The fraction of oil used had a sp. gr. 1·0254 at 20°, $a_D - 0{\cdot}68°$ at 26° in a 2 cm. tube, and distilled between 272° and 340° under the ordinary pressure. It contained free *n*-heptoic acid and palmitic acid, eugenol, asarylaldehyde, of which the oxime was also prepared and analysed, and esters of acetic and palmitic acids. From the fractions of high boiling point of the saponified oil a solid substance was isolated which separated in needle-shaped crystals, was crystallised from alcohol, and melted at 168°; for this substance, which has been observed by Schimmel & Co. (Schimmel's, *Ber.*, Oct., 1899, 8) and by Soden and Rojahn (Abstr., 1901, i, 395), the name *calameon* is proposed. Subsequent addition to the oils of moist ether or light petroleum caused the separation of a considerable quantity of asarone from which asarylaldehyde and asaronic acid were prepared; the amount of asarone in the oil can be directly deduced from the Zeisel methyl number, for none of the other constituents contains a methoxy-group.

By the action of arsenic acid on the fractionated oil, a solid arsenate was produced from which, after removing the arsenic, a polymeride of asarone was isolated; this was obtained as a white powder, consisting of minute, clear, transparent prisms, which melts at 203°, and distils with much decomposition between 175° and 225° under 16 mm. pressure; it can be prepared directly from pure asarone by the action of arsenic acid. It yields the same oxidation products as, and is partially reconverted into, asarone when distilled; its molecular weight corresponds with that required for the formula $(C_{12}H_{16}O_3)_3$, and the name *para-asarone* is suggested for the compound. After removing the whole of the asarone by this method or by means of sulphuric acid, a residue of hydrocarbon was left; the fractions of high boiling point contained a lævorotatory *hydrocarbon*, $C_{15}H_{22}$, which had a sp. gr. 0·9336 at 22°, and $[\alpha]_D - 13·38°$ at 22°, whilst the fractions of low boiling point gave a dextrorotatory hydrocarbon which had a sp. gr. 0·9330 at 18°, and $[\alpha]_D + 13·83°$ at 18°; the hydrocarbon could also be directly isolated by dissolving the fraction of the oil in light petroleum, treating with dry hydrogen chloride which precipitates the asarone and converts the hydrocarbon into the *hydrochloride*, $C_{15}H_{22},HCl$, which remains in solution and is left as a liquid on evaporating the solution; from this the hydrogen chloride is removed by distillation in a vacuum. T. M. L.

Calameon from Calamus Oil. By HERMANN THOMS and R. BECKSTROEM (*Ber.*, 1902, **35**, 3195—3200).—*Calameon*, $C_{15}H_{26}O_2$, separated from the fractions of high boiling point of calamus oil, forms glistening, hemihedral, orthorhombic crystals, melts at 168°, dissolves in 22 parts of cold alcohol, sublimes in glistening needles when heated, and has $[\alpha]_D -8·94°$ at 26° in alcohol; it is not an acid, phenol, aldehyde, ketone, ester, alcohol, or phenol ether, is not attacked by sodium in alcoholic solution, but in ethereal solution yields a *sodium* derivative, $C_{15}H_{25}O_2Na$, which forms a white, sandy precipitate, decomposes and becomes brown at 168°, and when boiled with water is reconverted into calameon.

Calameonic acid, $C_{15}H_{24}O_4,H_2O$, prepared by oxidising calameon with permanganate, crystallises from much ether in stout prisms, and melts with liberation of gas at 153°; the anhydrous substance crystallises from ether and melts at 138°. The *ammonium* salt, $C_{15}H_{23}O_4NH_4,1\frac{1}{2}H_2O$ melts at 180°. The *calcium* salt, with $6H_2O$, crystallises in glistening flakes. Carbon dioxide, and acetic and oxalic acids are also formed in small quantities in the oxidation.

Calameon combines additively with two atomic proportions of bromine, but the compound is not stable, loses water and hydrogen bromide, leaving an oil of the formula $C_{15}H_{21}Br$. By passing dry hydrogen chloride into an ethereal solution of calameon, a *hydrochloride*, $C_{15}H_{26}O_2,HCl$, is formed, which separates in white, needle-shaped crystals, melts at 119°, and is reconverted into calameon when boiled with alcohol.

When warmed with 80 per cent. sulphuric acid, acetyl chloride, or benzoyl chloride, calameon loses $2H_2O$ and leaves a hydrocarbon, *calamene*, $C_{15}H_{22}$; this is a clear, refractive liquid, boils at 144° under 15·5 mm. pressure, has a sp. gr. 0·9324 at 23°, and $[\alpha]_D -11·31°$ at 26°, is not reduced by metallic sodium, but combines with water when warmed with a mixture of sulphuric and acetic acids. By the action of bromine, a *substitution* product, $C_{15}H_{21}Br$, is obtained as a pale-yellow oil. Calamene gives a crystalline *hydrochloride* which melts at 108°. On oxidation, it is converted completely into acetic and oxalic acids. T. M. L.

Oil of Milfoil. By A. B. AUBERT (*J. Amer. Chem. Soc.*, 1902, **24**, 778—780).—This essential oil is of a dark bluish-green colour, and possesses a pleasant odour. It has a sp. gr. 0·9217 at 22°, n_D 1·506 at 20°, is miscible with absolute alcohol, ether, xylene, or chloroform, but only partially soluble in 95 per cent. alcohol. It was separated by distillation under reduced pressure into the following fractions, 170—190° (7 per cent.), 190—210° (17 per cent.), 210—220° (50 per cent.), 220—235° (9 per cent.), and above 235° (3 per cent.), leaving 14 per cent. of a dark coloured, waxy residue. The first fraction was slightly acid; it gave indications of the presence of a small amount of cineol (?) and of an aldehyde with an odour of cedar-wood.

The fraction 210—220° had at first a deep blue colour, but became light yellow when left in the dark. It consists principally of a substance having the composition $C_{12}H_{20}$, which is optically active, having a rotation $-14·2°$ in a 100 mm. tube, n_D 1·492, and boils at 254° (uncorr.) under 754·8 mm. pressure. When treated with bromine, it evolves hydrogen bromide and is converted into a pitch-like resin. T. A. H.

Chinese Oil of Neroli. By JOHN C. UMNEY and C. T. BENNETT (*Pharm. J.*, 1902, [iv], **15**, 146—147).—A sample of Chinese oil of neroli, said to have been obtained from *Citrus triptera*, had a yellowish-brown colour with a slight blue fluorescence, sp. gr. 0·850 at 15°, and optical rotation $+35°$ in a 10 cm. tube. It contained 4·79 per cent. of esters (calculated as linalyl acetate) and 21·41 per cent. of free alcohols (calculated as linalool). By distillation under the ordinary pressure, the following fractions were obtained: 170—175°, 30 per cent.; 175—180°, 14 per cent.; 180—185°, 21 per cent.; 185—190°, 7 per cent.; above 190°, 28 per cent. The chief constituents of the oil are limonene, camphene (?), linalool, linalyl acetate (traces), methyl anthranilate, and a paraffin hydrocarbon. E. G.

Chemistry of India-rubber. By CARL D. HARRIES (*Ber.*, 1902, **35**, 3256—3266).—When gaseous nitrous acid is passed through a benzene solution of Para rubber, a green, colloidal precipitate of the nitrosite, $(C_{10}H_{16}O_8N_2)_x$, separates, which is insoluble in all the common solvents except pyridine and aniline, which appear to decompose it. When this is further treated in suspension in benzene with nitrous acid, it changes to a yellow nitrosite (*nitrosite b*) which is soluble in ethyl acetate, acetone, or alkali solution, reduces Fehling's solution and decomposes when heated at 130°; from ebullioscopic measurements in acetone solution, its molecular weight has been found to be about 600 and its formula is $C_{20}H_{30}O_{16}N_6$. When oxidised with nitric acid, this nitrosite gives a dark yellow powder of the formula $C_{20}H_{31}O_{14}N_5$, oxalic acid, and an oil which appears to contain an aliphatic nitro-acid. When oxidised with permanganate, *nitrosite b* gives a mixture of fatty acids, principally oxalic and succinic.

When Para rubber is dissolved in moist benzene and a rapid current of unwashed nitrous acid is passed through the solution, another yellow powder is obtained, which has the formula $C_{20}H_{30}O_{14}N_6$, and is termed *nitrosite c*. This decomposes at about 160°, and on oxidation gives products similar to those obtained from *nitrosite b*.

Myrcene (from Bay oil) polymerises to a thick, greenish oil when heated for 4 hours at 300°. On subjecting the product to fractional distillation at a pressure of 13 mm., about a third passed over between 160° and 200°, and this was found to be *dimyrcene*. The undistilled residue consists of *polymyrcene*, which is soluble in benzene. By the action of nitrous acid on dimyrcene, a nitrosite is produced which is apparently identical with *nitrosite c* obtained from rubber. From the polymyrcene, a nitrosite of the formula $C_{40}H_{56}O_{18}N_6$ was formed.

The author has examined the products of the direct oxidation of Para rubber with nitric acid and confirms the observations made by Dittmar (this vol., i, 386). The "dipentene fraction" of rubber oil has been distilled under reduced pressure and the fractions examined as to density and refractive power; the results indicate the presence of a new hydrocarbon.

The results of the investigation tend to confirm Weber's opinion (Abstr., 1900, i, 353) that rubber is a derivative of an aliphatic terpene, that is, it is an unsaturated open-chain hydrocarbon.

J. McC.

Elemi. By ALEXANDER TSCHIRCH and J. CREMER (*Arch. Pharm.*, 1902, **240**, 293—324).—Forty-six specimens of elemi were examined, some partly crystalline, others amorphous. They were all derived from *Bursaraceae* or *Rutaceae*, and may be referred to three main types, derived from *Canarium*, *Amyris*, and *Protium* respectively. A sample of each of these types was examined chemically.

Manila elemi, from *Canarium commune.*—A specimen of soft resin was examined first; it had an acid number 21 and a saponification number 31·5. One per cent. aqueous ammonium and sodium carbonate solutions extract nothing from an ethereal solution of the resin. One per cent. aqueous potassium carbonate solution extracts acids, and α-manelemic acid, $C_{37}H_{56}O_4$ (Buri, Abstr., 1878, 439), crystallises from a solution of these in alcohol. This melts at 215°, has a specific rotation $[\alpha]_D$ 15·0°, acid number 104·5, corresponding with monobasicity, and "saponification" number 197; the last number really indicates the formation of a dipotassium salt, and is not a true saponification number, for mineral acids precipitate the original acid from the alkaline solution. The (mono) *potassium* and *silver* salts were analysed; (mono) *acetyl* and *benzoyl* derivatives were prepared, melting at 205° and 210° respectively; no methoxyl group is present; concentrated nitric acid oxidises the acid, forming a *substance* with the composition $C_{35}H_{54}O_{20}$, together with some picric acid. From the mother liquor of the α-acid, amorphous *β-manelemic acid*, $C_{44}H_{80}O_4$, was isolated; it melts at 75—76°, is optically inactive, and has an acid number 93 corresponding with monobasicity, and a saponification number 115. Manamyrin, $C_{30}H_{50}O$ (Vesterberg, Abstr., 1887, 733; 1891, 165), was obtained from the resin, freed from acid, by digesting it with alcohol and crystallising the residue from a mixture of alcohol and ether. This was benzoylated, and the product separated by means of hot 80 per cent. alcohol into a soluble and an insoluble portion melting at 191—192° and 228—229° respectively; by hydrolysis of these, α- and β-amyrin were prepared respectively, the latter with more difficulty; they melt at 181° and 192° and have the specific rotations 91·6° and 99·6°. Bryoidin, $C_{21}H_{42}O_3$, melting at 135·5°, was prepared by digesting the elemi with dilute alcohol at a gentle heat and evaporating the extract to crystallisation (Flückiger, *Buchner's Rep. Pharm.*, 224); from the mother liquor, a *bitter substance* and sodium chloride were obtained, the latter originating presumably from melting of the resin, when gathered, with boiling sea-water. By distilling the resin with steam, an *essential oil* was obtained and fractionated; one fraction boiled at 170—175° and had sp. gr. 0·955, another boiled at 175—210°, and eventually deposited a few crystals melting at 170°. *Maneleresen*, $C_{15}H_{30}O$, remains after the removal of the other constituents of the resin; it is amorphous and melts at 63—65°. In 100 parts of the drug there are contained: manamyrin, 20—25; essential oil, 20—25; bryoidin, 0·8—1; α-manelemic acid, 5—6; β-manelemic acid, 8—10; maneleresen, 30—35; inorganic constituents and bitter substance, 1—2; impurities, 5—6.

A specimen of hard resin was then examined. It had an acid number 24 and a saponification number 34, and resembled the soft resin, except that it contained more impurities and much less essential oil; the amount of α-manelemic acid slightly exceeded that of the β-acid.

A third specimen, collected from *Canarium commune*, was examined finally; it contained the same constituents as the other specimens.

Yucatan elemi, from *Amyris elemifera*.—The acid number of the specimen examined was 15, the saponification number 33. The constituents were much the same as in the Manila specimens, except that no acids were present. In 100 parts of the drug, there were contained: yucamyrin (melting at 179° and containing about equal parts of the α- and β-modifications), 10—15; essential oil, 8—10; yuceleresen (melting at 75—77°), 60—70; bitter substance and impurities, 4—5. The very large proportion which this resin contains of substances which resist the action of alkalis (resen and amyrin) makes it peculiarly suitable for the basis of a lacquer.

African (Cameroon) elemi, possibly from *Canarium Schweinfurthii*.—The acid number of the specimen examined was 24, the saponification number 38. Only an amorphous *afelemic acid*, $C_{44}H_{90}O_4$, was obtained: it melted at 97—98° and had an acid number 85, corresponding with monobasicity, and a saponification number 102. *Afamyrin* melted at 170° and was not separated into constituents. No bryoidin was found. In 100 parts of the drug there were contained: afamyrin, 20—25; essential oil, 15—20; afelemic acid, 8—10; afeleresen, 40—45.

Brazilian Protium-Elemi (*Almessega-Elemi*), from *Almessega brancha*.—A small specimen of this rare elemi was examined; it had an acid number 32 and a saponification number 54·5. The resin contained one-fourth of its weight of impurities; when freed from these, it was found to contain in 100 parts: *protamyrin*, $C_{30}H_{50}O$ (melting at 170—171°), 30; amorphous *protelemic acid*, 25; *proteleresen*, 37·5. Only traces of essential oil and of bitter substance were present, and bryoidin could not be detected.

It is noteworthy that all the five samples of elemi examined, although they were not derived from the same genus of plants, or even from the same family, yet contained an amyrin—that is, a mixture of two isomeric alcohols with the composition $C_{30}H_{50}O$. In the future, Tschirch proposes to regard as elemis proper only those which contain amyrin or an allied substance.

C. F. B.

Soluble Hydroxyanthraquinone-glucoside contained in Barbadoes Aloes. By EUGEN AWENG (*Chem. Centr.*, 1902, ii, 368—369; from *Apoth.-Zeit.*, 17, 422).—A large quantity of a double glucoside which resembles that contained in *Frangula* and *Sagrada* (Abstr., 1901, i, 39) has been isolated from the aqueous extract of Barbadoes aloes. This compound gives the reactions of hydroxyanthraquinone and when boiled with hydrochloric acid forms sugar and a substance similar to the ψ-emodin obtained from *Frangula*. A considerable quantity of ψ-emodin may also be extracted from the aloes by treating the portion insoluble in water with 95 per cent. alcohol. By the action of bromine or by boiling this ψ-emodin with alcohol and acid for a long time, emodin and a compound which gives the reactions of rhamnetin are formed. E. W. W.

Extractum Filicis. By FRIEDRICH KRAFT (*Chem. Centr.*, 1902, ii, 533—534; from *Schweiz. Woch. Pharm.*, 40, 322—326. Compare Abstr., 1898, i, 40; 1899, i, 32; 1900, i, 49).—Good extracts prepared from the roots of *Aspidium Filix-mas.* contained on the average 3·5 per cent. of filicic acid, 2·5 of flavaspidic acid, 0·05 of albaspidin, 0·1 of aspidinol, 0·1 of flavaspidin, 5 of amorphous acid, and 6 of filicinigrin. Flavaspidic acid may be extracted from crude filicic acid by means of carbon disulphide; it dissolves in 30 parts of hot disulphide, and on cooling 85 per cent. crystallises out. Flavaspidin resembles flavaspidic acid very closely and a small quantity is generally contained in the acid. It is, however, less soluble in carbon disulphide than the acid, crystallises from ethyl acetate in colourless prisms, melts at 199°, and is readily soluble in benzene, chloroform, acetone, or amyl alcohol; it dissolves in alkalis and decomposes carbonates of alkalis or alkaline earths. Filicinigrins consist of decomposition products of the other six components of the extract and form a brown to black, amorphous powder; they are distinguished from the other acids by their insolubility in light petroleum and their physiological inactivity; their solubility is variable and sometimes the powder is infusible.

The chief component of the extract is the amorphous acid, and on this its pharmacological effect depends. It forms a brownish-yellow, amorphous powder, melts at about 60°, is very readily soluble in acetone, chloroform, ethyl acetate, ether, benzene, carbon disulphide, carbon tetrachloride, or glacial acetic acid. The slight reduction effected by boiling the acid with ammoniacal silver solutions or with Fehling's solution is probably due to the presence of decomposition products. Ferric chloride precipitates an amorphous, reddish-brown substance from the alcoholic solution. When melted with alkalis, the acid yields the same products as filicic acid (Boehm) together with methylphloroglucinol methyl ether melting at 118—119° and an acid melting at 137°. The amorphous acid must therefore possess a more complicated structure than filicic acid and may possibly be a homologue containing four butanone rings. E. W. W.

Reduction of Artemisin by means of Stannous Chloride. By P. BERTOLO (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 486—492. Compare Abstr., 1901, i, 718).—In order further to study the analogy in behaviour existing between santonin and artemisin, the author has investigated the reduction of the latter by means of stannous chloride in hydrochloric acid solution. Instead, however, of yielding a compound analogous with santonous acid, this reduction furnishes a product possessing a lactonic structure and having the composition $C_{15}H_{18}O_3$, the same as that of santonin. This *compound* crystallises from alcohol or acetic acid in small, white needles which melt at 269—270° and are slightly soluble in ether, chloroform, benzene, or aqueous alkalis; when suspended in water and treated with ferric chloride or sulphuric acid, it is turned brown, but remains undissolved. On boiling with solutions of the alkalis or alkaline earths, the compound yields salts of a monobasic hydroxy-acid; the *barium*, $(C_{15}H_{19}O_4)_2Ba$, *silver*, *lead*, and *copper* salts were prepared; when treated with hydrochloric or sulphuric acid, these salts are slowly converted into the original lactonic compound. The *acetyl* derivative of the latter, $C_{15}H_{17}O_3Ac$, crystallises from alcohol, or from a mixture of chloroform or benzene with light petroleum, in white, shining leaflets or needles which melt at 205—206°; on boiling with potassium hydroxide solution and acidifying with hydrochloric acid, the original lactone is re-formed.

These results show that, in place of the carbonyl group present in artemisin, the reduction product of the latter contains a hydroxyl group of a phenolic nature. When fused with alkali, the compound yields 1 : 4-dimethyl-β-naphthol; this compound is not obtained either from santonin or artemisin and the author concludes that the ketonic groups in the molecules of these two substances occupy corresponding positions.

On reducing artemisin by means of zinc dust and acetic acid, a dextrorotatory *compound* of a lactonic nature melting at 275° is obtained.

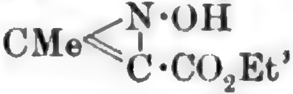
When artemisin is treated with sodium carbonate and the solution acidified with dilute sulphuric acid, a compound is obtained crystallising from water in long, silky needles which melt at 121—122° and in alcoholic solution are dextrorotatory. T. H. P

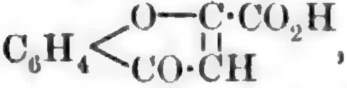
Degradation of Brazilin. By WILLIAM H. PERKIN, jun. (*Ber.*, 1902, **35**, 2946—2947).—A claim of priority (see Proc., 1902, **18**, 147) over Kostanecki and Paul (this vol., i, 686). R. H. P.

Dyeing of Animal Fibres by Acid Colouring Matters. By PAUL SISLEY (*Bull. Soc. Chim.*, 1902, [iii], **27**, 901—914).—The author determines the partition coefficient of picric acid between water and toluene, water and ether, and water and amyl alcohol, and shows that in all these cases the partition coefficient depends on the concentration. Similar results were obtained with various acid colouring matters. Experiments were also carried out on the extraction of picric acid both in neutral and in acid solution by silk, amyl alcohol, and toluene, when it was found that the amount of picric acid extracted was much greater in acid solution than in neutral. This the author explains by the diminution of the dissociation of picric acid by the acid added.

[No reference is made to the work of Walker and Appleyard (Trans., 1896, **69**, 1334) on this subject.] A. F.

Composition of the Tanning Material 'Taran.' By F. Sarosek (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 504).—Taran is a root used for tanning in the native tanneries of Central Asia; it contains 17 per cent. of tannin which is taken up by leather; ellagic acid is also present. T. H. P.

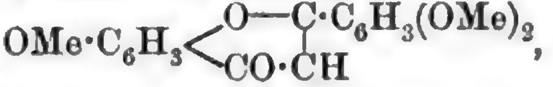
Action of Hydroxylamine on Ethyl Dimethylpyronedicarboxylate. By Carlo Palazzo (*Atti R. Accad. Lincei*, 1902, [v], **11**, i, 562—565).—The action of hydroxylamine on the ethyl dimethylpyronedicarboxylate prepared by Conrad and Guthzeit (Abstr., 1886, 333) in presence of sodium carbonate yields a *compound* which has probably the constitution  $\mathrm{CMe}\!\left<\begin{array}{l}\mathrm{N{\cdot}OH}\\ \mathrm{C{\cdot}CO_2Et}\end{array}\right.$, and separates from water in shining, white needles containing water of crystallisation; it is soluble in acetone, hydrochloric acid, or acetic acid, and in acetic acid solution gives the normal depression of freezing point. The anhydrous compound melts at 164° and immediately afterwards undergoes vigorous decomposition. It decolorises permanganate in the cold and in acetic acid solution absorbs bromine, whilst when heated with hydriodic acid, it evolves ethyl iodide. With silver nitrate, it gives a white precipitate, which has the composition $C_6H_8O_3NAg,2H_2O$, and is rapidly turned violet by the action of direct sunlight. T. H. P.

Chromone. By R. Heywang and Stanislaus von Kostanecki (*Ber.*, 1902, **35**, 2887—2891. Compare Abstr., 1901, i, 735; and this vol., i, 303, 690).—Chromone derivatives have been prepared (*loc. cit.*) by condensing derivatives of *o*-hydroxyacetophenone and ethyl oxalate. Ruhemann and Stapleton (Trans., 1900, **77**, 1179) prepared chromone itself from phenoxyfumaric acid. Chromone-2-carboxylic acid,  $\mathrm{C_6H_4}\!\left<\begin{array}{l}\mathrm{O{-}C{\cdot}CO_2H}\\ \mathrm{CO{\cdot}CH}\end{array}\right.$, has now been prepared from *o*-hydroxyacetophenone, ethyl oxalate, and sodium; the ethyl *o*-hydroxybenzoylpyruvate first formed was not purified, but converted into chromone-2-carboxylic acid by treatment with hydrogen chloride in alcoholic solution; the acid crystallised in needles decomposing at 252° (compare Ruhemann and Stapleton) with evolution of carbon dioxide and formation of chromone. Chromone is decomposed by boiling with alcoholic sodium ethoxide into *o*-hydroxyacetophenone and formic acid.

The melting point of α-naphthachromone (this vol., i, 303), which has not been previously recorded, is 125°.

The paper contains a list of the chromone derivatives which up to the present time have been prepared. K. J. P. O.

3 : 3′ : 5′-Trihydroxyflavone. By Stanislaus von Kostanecki and Peter Weinstock (*Ber.*, 1902, **35**, 2885—2887).—2 : 4-*Diethoxy*-3′ : 5′-*dimethoxybenzoylacetophenone*, $C_6H_3(OEt)_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}C_6H_3(OMe)_2$, is prepared by heating 2 : 4-diethoxyacetophenone and ethyl 3 : 5-dimethoxybenzoate with sodium at 130°, it crystallises in needles melting at 139·5°, and gives a dirty red coloration with ferric chloride. When the β-diketone is boiled with hydriodic acid, it is converted into trihydroxyflavone, which, for purposes of purification, is methylated by means of methyl sulphate and potassium hydroxide.

3 : 3′ : 5′-*Trimethoxyflavone*,  $\mathrm{OMe{\cdot}C_6H_3}<\begin{array}{l}\mathrm{O{-}C{\cdot}C_6H_3(OMe)_2}\\ \mathrm{CO{\cdot}CH}\end{array}$, crystallises in needles melting at 181—182°, and by prolonged boiling with hydriodic acid is converted into 3 : 3′ : 5′-*trihydroxyflavone*,

$$C_{15}H_7O_2(OH)_3\,;$$

the latter forms crusts of microscopic needles melting at 329°, dissolves in sodium hydroxide with a greenish-yellow coloration, and in concentrated sulphuric acid with a yellow coloration and a greenish fluorescence. 3 : 3′ : 5′-*Triacetoxyflavone*, $C_{15}H_7O_2(OAc)_3$, crystallises in white needles melting at 187°. K. J. P. O.

Hyoscine and Atroscine. By OSWALD HESSE (*J. pr. Chem.*, 1902, [ii], **66**, 194—205. Compare this vol., i, 51).—Freshly prepared hyoscine hydrobromide has $[\alpha]_D$ − 27·7° at 15°; after four weeks, the rotation has diminished to $[\alpha]_D$ − 25·9°. This is probably due to the existence of a labile modification of hyoscine.

Atroscine occurs in a crystalline and an amorphous form. The latter is obtained on separation of the alkaloid from its salts, or from the crystalline form when placed over concentrated sulphuric acid or phosphoric acid. Atroscine monohydrate and dihydrate crystallise together on addition of a crystal of each to the syrupy atroscine at 5—8°. At 0° the dihydrate, at 15—20° the monohydrate, is formed. In presence of a trace of the monohydrate at 20°, the dihydrate changes slowly to the monohydrate; the change takes place more quickly in contact with ether at 15°. When pure, the dihydrate is not less stable than the monohydrate (compare Gadamer, this vol., i, 173; Kunz-Krause, this vol., i, 174).

When molecular proportions of tropine platinichloride and oscine platinichloride (m. p. 210—212°) are dissolved together in hot water, dark orange-red crystals, $(C_8H_{15}ON,C_8H_{13}O_2N)_2,H_2PtCl_6$, separate which contain no water of crystallisation, melt and decompose at 202—204°, and are probably identical with Ladenburg's ψ-tropine platinichloride (this vol., i, 390). The remainder of the paper is a reply to E. Schmidt's note to Gadamer's paper. G. Y.

β-Methylmorphimethine. By LUDWIG KNORR and SAMUEL SMILES (*Ber.*, 1902, **35**, 3009—3010. Compare Abstr., 1894, i, 430).—β-Methylmorphimethine is formed when the α-compound is boiled with acetic anhydride, water, or 50 per cent. alcohol, but not with absolute alcohol. It is best prepared by boiling the α-compound with 60 per cent. alcohol containing 10 per cent. of potassium hydroxide, and crystallises in prisms melting at 134—135°; $[\alpha]_D$ + 438° ($c = 1$) in solution in 97 per cent. alcohol. The base forms a violet solution in sulphuric acid, which becomes blue and then green when ice-water is added. The *methiodide* melts at about 300° and has $[\alpha]_D$ + 233° ($c = 0·6$) in solution in 97 per cent. alcohol. The *benzoate* crystallises in small needles melting at 157° and has $[\alpha]_D$ +254° ($c=1$) in aqueous solution. The oily base, as obtained by the action of acetic anhydride on the α-compound, can be readily purified by means of the benzoate.

A. H.

A Fourth Methylmorphimethine. By LUDWIG KNORR and JOHN HAWTHORNE (*Ber.*, 1902, **35**, 3010—3013. Compare the preceding abstract).—γ-Methylmorphimethine (Schryver and Lees, Trans., 1901, **79**, 563) is converted by boiling alcoholic potash into *δ-methylmorphimethine*, which crystallises in prisms melting at 111—113° and has $[\alpha]_D$ +256·6° ($c=1{\cdot}243$) in solution in methyl alcohol. The base is as a rule more readily soluble than the γ-isomeride. The *methiodide* of *δ-methylmorphimethine* crystallises in rectangular plates which melt and decompose at about 282—284°; $[\alpha]_D$ +150·7° ($c=1{\cdot}003$) in absolute alcohol. This substance can also be obtained by heating the methiodide of the γ-base with dilute aqueous potash. The *benzoate* crystallises in slender needles, melts indefinitely at 99—108°, and has $[\alpha]_D$ +181·1° ($c=0{\cdot}6315$) in solution in 99 per cent. alcohol. *γ-Methylmorphimethine benzoate* also melts indefinitely at about 100°, is more readily soluble in water than the γ-derivative, and has $[\alpha]_D$ +41·3° ($c=0{\cdot}8685$) in solution in 99 per cent. alcohol.

A. H.

Morphigenine and Epiosine. By ERNST VAHLEN (*Ber.*, 1902, **35**, 3044—3047. Compare *Arch. Path. Pharm.*, **48**, 368).—In reply to the criticism of Pschorr (this vol., i, 672), the author maintains that the physiological action of epiosine resembles that of morphine and is not due to the formation of methæmoglobin in the blood of the animals experimented on.

A. H.

Addition of Sulphurous Acid on Quinidine. By WILHELM KÖNIGS and HANS SCHÖNEWALD (*Ber.*, 1902, **35**, 2980—2991).—An aqueous solution of quinidine, which has been saturated with sulphur dioxide, deposits, after some weeks, the monobasic *acid*, $C_{20}H_{26}O_7N_2S_2$; this crystallises with $4H_2O$ and decomposes at about 260°. Its solutions in dilute sulphuric acid exhibit a blue fluorescence and give the colorations with chlorine water and ammonia characteristic of quinine and quinidine. The *hydrobromide* and *hydrochloride* are both crystalline salts. The *ammonium* salt, with $4H_2O$, is amorphous, and has $[\alpha]_D$ 160°42′ at 19·5°. The *barium* and *silver* salts were obtained as yellow, amorphous precipitates, and the *monobromo*-derivative, $C_{20}H_{25}O_7N_2BrS_2$, as a pale yellow, crystalline precipitate. When oxidised with chromic acid, the acid yields quininic acid, and when oxidised with permanganate in the cold, the sulphonic *acid*, $C_{20}H_{28}O_8N_2S_2$, which crystallises with $4H_2O$ in beautiful, white, six-sided leaflets and forms a pale yellow, amorphous, hygroscopic *ammonium* salt.

Quinine yields the analogous additive *product*, $C_{20}H_{26}O_7N_2S_2,H_2O$, only in small quantities.

R. H. P.

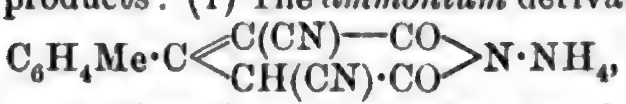
Pipecoline Derivatives. By G. VON OSTOJA BALICKI (*Ber.*, 1902, **35**, 2780—2782).—*Nitrosopipecoline* is an oil boiling at 123° under

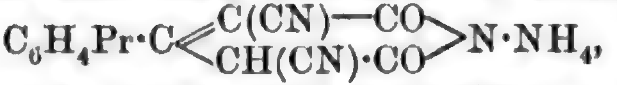
31 mm. pressure; it is prepared by treating a solution of pipecoline in cold dilute sulphuric acid with sodium nitrite. On reduction with zinc dust and water, the nitrosoamine yields *pipecolylhydrazine* (1·*aminopipecoline*); this product is a colourless oil boiling at 156—160° which has a sp. gr. 0·90058 at 19°/4°. The *s*-hydrazine solidifies, on cooling, in solid carbon dioxide and yields uncrystallisable salts with halogen hydracids; the *picrate* crystallises from alcohol in orange-yellow needles and melts at 143°.

A crystalline *hydrazone*, $C_6H_{12}N\cdot N:CH\cdot C_6H_4\cdot NO_2$, melting at 63°, was obtained from the hydrazine and *m*-nitrobenzaldehyde, but benzaldehyde, piperonaldehyde, acetone, and acetophenone yield oily hydrazones, and dextrose furnishes only an uncrystallisable osazone.

G. T. M.

Condensation of Aldehydes with Ethyl Cyanoacetate. I. By Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1901—1902, **37**, 593—611. Compare Abstr., 1900, i, 52 and 111).—The author has shown (*loc. cit.*) that the reaction between an aldehyde, ethyl cyanoacetate, and ammonia leads, not to a piperidine derivative, as was to be expected, but to a pyridine compound, there being an apparent disappearance of hydrogen. The latter the author has now traced, and he finds that it is used up in converting some of the cyanoacetamide derivative, which is an intermediate product in the above reaction, into the corresponding saturated compound. These reactions are expressed by the equations: (1) $R\cdot CHO + CN\cdot CH_2\cdot CO_2Et + NH_3 = Et\cdot OH + H_2O + R\cdot CH:C(CN)\cdot CO\cdot NH_2$. (2) $R\cdot CH:C(CN)\cdot CO\cdot NH_2 + H_2 = R\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2$. This reaction may also be employed to obtain, not only dicyanodioxypyridines, but also monoalkylcyanoacetamides. The reactions of certain other aldehydes with ammonia and ethyl cyanoacetate have been studied, the results being as follows:

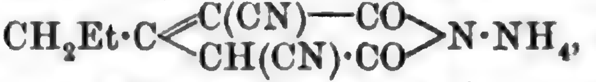
m-Tolualdehyde, ammonia, and ethyl cyanoacetate give rise to three products: (1) The *ammonium* derivative of m-*tolyldicyanoglutaconimide*,  $C_6H_4Me\cdot C\left<\begin{matrix}C(CN)-CO\\ CH(CN)\cdot CO\end{matrix}\right>N\cdot NH_4$, the main product of the reaction, crystallises from water in colourless, anhydrous needles which are soluble in pyridine and do not melt even at 290°; when heated with 60 per cent. sulphuric acid, it yields *m*-tolyl-γ-cyanovinylacetic acid, $C_6H_4Me\cdot C(:CH\cdot CN)\cdot CH_2\cdot CO_2H$, to be described in a later communication; the *silver* and *copper* ($+6H_2O$) salts were prepared. (2) m-*Tolylcyanoacetamide*, $C_6H_4Me\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2$, crystallises from water in broad, nacreous laminæ which melt at 108·5—109·5°, and are soluble in alcohol, ether, or pyridine. (3) A compound almost insoluble in water and melting, in the crude condition, at 194—198°.

Cuminaldehyde, ammonia, and ethyl cyanoacetate yield two products: (1) The *ammonium* derivative of *propylphenyl-ββ-dicyanoglutaconimide*,  $C_6H_4Pr\cdot C\left<\begin{matrix}C(CN)-CO\\ CH(CN)\cdot CO\end{matrix}\right>N\cdot NH_4$, crystallising from water in yellowish, slender needles, dissolving in alcohol or pyridine, and remaining unfused at 290°; when heated with 60 per cent. sulphuric acid, it yields β-propylphenyl-γ-cyanovinylacetic (cumyl-γ-cyanovinylacetic acid), to be described in another communication. The *copper*

$(+8H_2O)$ and *silver* salts were prepared and analysed. The *coniine* derivative, $C_{16}H_{13}O_2N_3,C_8H_{17}N$, is precipitated either in prisms or needles melting at 251—252°; the *nicotine* salt forms a minutely crystalline precipitate melting at about 300°. (2) *Cumylcyanoacetamide* (α-cyanopropylphenylhydrocinnamamide),

$$C_6H_4Pr\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2,$$

separates from water in long, colourless, silky needles which are soluble in alcohol or pyridine and melt at 144—145°; it sublimes, but with partial decomposition. Its solution is neutral and develops ammonia when heated with potassium hydroxide.

n-Butaldehyde, ammonia, and methyl (or ethyl) cyanoacetate interact with the formation of: (1) The *ammonium* derivative of *propyldicyanoglutaconimide*,  $CH_2Et\cdot C{<}\begin{matrix}C(CN)—CO\\CH(CN)\cdot CO\end{matrix}{>}N\cdot NH_4$, which separates from water in slender, silky needles soluble in pyridine; it has a bitter taste, recalling those of quinine and magnesium sulphate. When heated with 60 per cent. sulphuric acid, it yields β-propyl-γ-cyanovinylacetic acid, to be described later; the silver salt was prepared. (2) *Butylcyanoacetamide* (β-propyl-α-cyanopropionamide),

$$CHPr\cdot CH(CN)\cdot CO\cdot NH_2,$$

which crystallises from water in thin, nacreous laminæ melting at 125·5—126·5° and subliming in iridescent plates; it gives a neutral aqueous solution, is soluble in pyridine, and yields ammonia when heated with potassium hydroxide solution.

Benzaldehyde, ammonia, and ethyl cyanoacetate yield (1) benzylcyanoacetamide, (2) phenyldicyanodioxypyridine (*loc. cit.*), and (3) a compound, insoluble in water and probably identical with that of Carrick.

Anisaldehyde, ammonia, and ethyl cyanoacetate yield *anisylcyanoacetamide*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH(CN)\cdot CO\cdot NH_2$, which crystallises from ether in slender, silky needles soluble in water or alcohol and melting at 172°.

From heptaldehyde, ammonia, and ethyl cyanoacetate are obtained the two products: (1) the ammonium derivative of γ-hexyl-ββ-dicyanodioxypyridine, and (2) heptyl-α-cyanoacetamide, which will be described in a later communication.

T. H. P.

Action of Sulphuryl Chloride on Pyrrole. By GIROLAMO MAZZARA (*Gazzetta*, 1902, **32**, i, 510—514).—The interaction of 1 mol. of sulphuryl chloride and 1 mol. of pyrrole yields an unstable *monochloro*-derivative of the latter, which is a heavy, yellow liquid and decomposes explosively, whilst with 2 mols. of the chloride a *dichloro*-compound is obtained which, when repeatedly distilled in a current of steam, is converted first into a white, buttery mass and afterwards into carbonaceous matter. Both these compounds are volatile in a current of steam and colour sulphuric acid green, whilst pine shavings moistened with hydrochloric acid are turned red by them.

Tetrachloropyrrole, C_4NHCl_4, is obtained in good yield by the interaction at 0° of an absolute alcoholic solution of pyrrole with sulphuryl chloride (4 mols.), and is identical with Ciamician and Silber's (Abstr., 1885, 1077) compound.

T. H. P.

Formation of Pyrrole Derivatives from *iso*Nitrosoketones. By Ludwig Knorr and H. Lange (*Ber.*, 1902, **35**, 2998—3008. Compare *Annalen*, 1886, **236**, 296).—Pyrrole derivatives have hitherto been obtained from three different *iso*nitroso-derivatives by reduction in presence of a ketone or ketonic ester, and the reaction has now been extended to four additional *iso*nitroso-compounds. The intermediate formation of amino-ketones is rendered probable by the fact that in many cases the substitution of aminoacetophenone for *iso*nitrosoacetophenone was accompanied by a considerable increase in the yield, whilst in certain cases pyrrole derivatives were obtained from the amino-ketone but not from the *iso*nitroso-ketone. In the new series of syntheses, the following results were obtained. *iso*Nitrosoacetophenone yields pyrrole derivatives with ethyl acetoacetate (the yield being 56 per cent.), acetylacetone (40 per cent.), ethyl acetonedicarboxylate (3 per cent.), benzoylacetone (4·5 per cent.), but does not yield them with ethyl oxalacetate, ethyl acetoneoxalate, dibenzoylmethane, formylacetone, phenylacetone, diphenylacetone, or acetophenone. Aminoacetophenone gives pyrrole derivatives with ethyl acetoacetate (almost 100 per cent.), acetylacetone (100 per cent.), ethyl acetonedicarboxylate (9 per cent.), benzoylacetone (38 per cent.), and in traces with ethyl acetoneoxalate, formylacetone, and phenylacetone, whilst it does not yield them with ethyl oxalacetate, dibenzoylmethane, benzoylaldehyde, diphenylacetone, and deoxybenzoin.

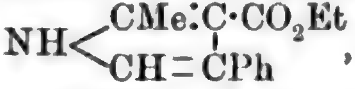
*iso*Nitrosodeoxybenzoin yields pyrrole derivatives with ethyl acetoacetate (25 per cent.) and with acetylacetone (50 per cent.), but not with deoxybenzoin.

*iso*Nitrosoacetone yields pyrrole derivatives with ethyl acetoacetate (50 per cent.), acetylacetone (33 per cent.), and in traces with benzoylacetone. Finally, dimethyl *iso*nitrosoacetonedicarboxylate yields a pyrrole derivative with dimethyl acetonedicarboxylate.

Acetone and methyl ethyl ketone with *iso*nitrosoacetone, and acetone with *iso*nitrosoacetophenone give products which only yield the reactions of pyrrole derivatives after treatment with strong sulphuric acid. These cases seem to indicate that the reaction proceeds in two stages.

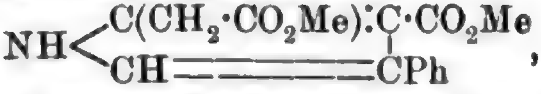
The following new compounds have been obtained by this method.

Ethyl 3-phenyl-5-methylpyrrole-4-carboxylate,



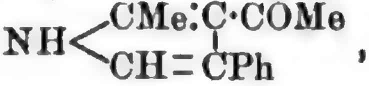
$$\mathrm{NH}<\begin{array}{l}\mathrm{CMe{:}C\cdot CO_2Et}\\ \mathrm{CH=CPh}\end{array},$$

is prepared from ethyl acetoacetate and *iso*nitrosoacetophenone or aminoacetophenone, melts at 105°, and gradually becomes yellow in the air. The corresponding *acid* melts and loses carbon dioxide at 115°. *Dimethyl 3-phenylpyrrole-4-carboxylo-5-acetate*,



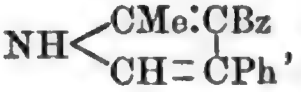
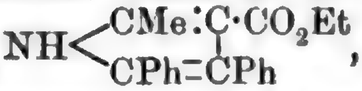
$$\mathrm{NH}<\begin{array}{l}\mathrm{C(CH_2\cdot CO_2Me){:}C\cdot CO_2Me}\\ \mathrm{CH=\!=\!=\!=\!=CPh}\end{array},$$

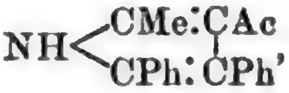
prepared from methyl acetonedicarboxylate and *iso*nitrosoacetophenone, melts at 126°. 4-*Acetyl-3-phenyl-5-methylpyrrole*,



$$\mathrm{NH}<\begin{array}{l}\mathrm{CMe{:}C\cdot COMe}\\ \mathrm{CH=CPh}\end{array},$$

prepared from *iso*nitrosoacetophenone and acetylacetone, melts at 151°, and is converted by the action of benzaldehyde and aqueous potash into 4-*cinnamoyl-3-phenyl-5-methylpyrrole* melting at 167°.

4-*Benzoyl-3-phenyl-5-methylpyrrole*,  $NH<\begin{array}{l}CMe{:}CBz \\ CH{=}CPh\end{array}$, prepared from *iso*nitrosoacetophenone and benzoylacetone, melts at 231°. *Ethyl* 2 : 3-*diphenyl-5-methylpyrrolecarboxylate*,  $NH<\begin{array}{l}CMe{:}C{\cdot}CO_2Et \\ CPh{=}CPh\end{array}$, prepared from ethyl acetoacetate and *iso*nitrosodeoxybenzoin, is a colourless, crystalline substance.

4-*Acetyl*-2 : 3-*diphenyl-5-methylpyrrole*,  $NH<\begin{array}{l}CMe{:}CAc \\ CPh{:}CPh\end{array}$, is prepared from acetylacetone and *iso*nitrosodeoxybenzoin, and is converted by benzaldehyde into 4-*cinnamoyl*-2 : 3-*diphenyl-5-methylpyrrole*, which melts at 215°.

The reaction product obtained from acetone and *iso*nitrosoacetone does not contain a pyrrole derivative, but one is formed when it is mixed with sulphuric acid. The expected dimethylpyrrole could not be obtained pure, a large proportion of dimethylpyrazine being simultaneously formed. A. H.

[Double Salts of Thallium and Alkaloids with Hydracids.] By CARL RENZ (*Ber.*, 1902, **35**, 2768—2774. Compare R. J. Meyer, Abstr., 1900, ii, 655, and this vol., i, 393).—*Thallic bromide pyridine hydrobromide*, $(TlBr_3)_2(C_5NH_5,HBr)_3$, obtained by dissolving the corresponding double chloride in hot concentrated potassium bromide solution, crystallises on cooling in pale yellow needles melting at 174°.

Thallic chloride piperidine hydrochloride, $TlCl_3(C_5NH_{11},HCl)_3$, unlike the other organic double salts of the type, is extremely soluble and separates from a concentrated solution of its generators only after further evaporation under reduced pressure; it forms long, prismatic crystals, soluble in alcohol but not in ether.

Thallic iodide hyoscyamine hydriodide, $TlI_3,C_{17}H_{23}O_3N,HI$, separates in red crystals from a concentrated solution of potassium iodide and the corresponding double chloride and melts at 200°.

Thallic iodide atropine hydriodide, $TlI_3,C_{17}H_{23}O_3N,HI$, resembles the preceding compound and melts at 192°.

Thallic chloride cocaine hydrochloride, $TlCl_3,(C_{17}H_{21}O_4N,HCl)_2$, resulting from the interaction of its generators in concentrated solutions, crystallises in white needles.

Thallic chloride strychnine hydrochloride, $TlCl_3,(C_{21}H_{22}O_2N_2,HCl)_2$, obtained like the preceding double salt, crystallises from a mixture of alcohol and dilute hydrochloric acid in iridescent leaflets decomposing at 240°.

Thallic chloride cinchonine hydrochloride,

$$TlCl_3,(C_{19}H_{22}ON_2,HCl)_2,4H_2O,$$

crystallises from hot dilute hydrochloric acid in aggregates of silky needles.

Thallic chloride quinine hydrochloride, $TlCl_3,C_{20}H_{24}O_2N_2,HCl,2H_2O$, closely resembles the preceding compound.

Thallic chloride yields less stable double salts with coniine, nicotine, and 2 : 6-lutidine; with morphine, it gives rise to an insoluble yellowish-white powder, $(TlCl_3)_6,C_{17}H_{19}O_3N$.

Dimethylaniline interacts with thallic chloride, giving rise to a violet colouring matter resembling crystal-violet; dimethyl-*o*-toluidine furnishes a similar dye of redder shade.

Methyldiphenylamine, when left in contact with an alcoholic solution of thallic chloride, becomes oxidised to a blue colouring matter which is probably identical with diphenylamine-blue. G. T. M.

The Three Isomeric Cyanides of Pyridine. By RUDOLF CAMPS (*Arch. Pharm.*, 1902, **240**, 366—370).—All three cyanopyridines can be obtained by distilling under diminished pressure a mixture of phosphoric oxide with the amide of the corresponding pyridinecarboxylic acids (this vol., i, 824). In the case of the 4-compound, it was found also that the cyanide can be obtained by distilling a mixture of the acid with lead thiocyanate.

2-Cyanopyridine is not reduced to pyridylmethylamine by 3 per cent. sodium amalgam; pyridine and hydrocyanic acid are formed, and at the same time a certain amount of hydrolysis to the amide and the acid takes place. Nor can 4-cyanopyridine be reduced with aluminium amalgam; the acid is formed.

Cyanopyridines (*pyridyl cyanides*), $C_5NH_4\cdot CN$.—The 2-compound (*picolinonitrile*) melts at 29°. The 4-isomeride (*isonicotinonitrile*) melts at 79°; its *hydrochloride*, *platinichloride*, and *aurichloride* melt and decompose at 199°, 293°, and 185° respectively; the *mercurichloride*, $C_5NH_4\cdot CN,HgCl_2$, was analysed. C. F. B.

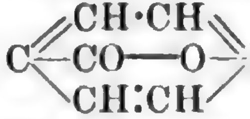
Ethyl 2:6-Dimethyl-4-chloronicotinate. By AUGUST MICHAELIS and R. HANISH (*Ber.*, 1902, **35**, 3156—3161).—The compound previously described as 2:6-dimethylchloroethoxylutidine (Abstr., 1901, i, 609) is now shown to be ethyl 2:6-dimethyl-4-chloronicotinate (compare Collie, Trans., 1891, **59**, 176).

The *aurichloride* of the ester melts at 116—117° and the *picrate* at 129°. Methyl iodide at 95—100° transforms the ester into *ethyl 2:6-dimethyl-4-iodonicotinate methiodide*, $C_{10}H_{12}O_2NI,MeI$, melting at 194°. Methyl bromide yields the *methobromide*, $C_{10}H_{12}O_2NCl,MeBr$, melting at 198°. Concentrated hydrochloric acid at 150° converts the ester into γ-lutidone melting at 224—225°. Aniline yields Conrad and Epstein's phenylaminolutidine (Abstr., 1887, 501). 4-Chloro-2:6-dimethylnicotinic acid melts at 168—170°, and when heated at 175° loses carbon dioxide and yields chlorolutidine. 4-*Ethoxy*-2:6-*dimethylnicotinic acid* crystallises from hot water in colourless needles containing $3H_2O$; when anhydrous, it melts at 200—201°. The *sodium* salt, *silver* salt, and the *hydrochloride* melting at 127° have been prepared. J. J. S.

Derivatives of 2:6-Dichloro*iso*nicotinic Acid. By KARL BITTNER (*Ber.*, 1902, **35**, 2933—2936).—2:6-*Dianilinopyridine-4-carboxyanilide*, $C_5NH_2(NHPh)_2\cdot CO\cdot NHPh$, prepared by heating dichloro*iso*nicotinic acid with aniline, crystallises from alcohol in olive-green, glistening, hexagonal plates and melts at 140—141°. The *acid*, $C_5NH_2(NHPh)_2\cdot CO_2H$, crystallises from alcohol in yellow, microscopic needles and does not melt at 300°. The *methyl* ester, $C_5NH_2(NHPh)_2\cdot CO_2Me$, crystallises from alcohol and melts at 142°.

2 : 6-*Dithiolpyridine-4-carboxylic acid*, $C_5NH_2(SH)_2\cdot CO_2H$, forms small, reddish-yellow needles and melts at 230°. The *potassium* salt, $KS\cdot C_5NH_2(SH)\cdot CO_2K,EtOH$, separates from alcohol in insoluble, glistening, golden flakes and does not lose its alcohol of crystallisation by long drying at 110°. The *methyl* ester, $C_5NH_2(SH)_2\cdot CO_2Me$, separates from dilute methyl alcohol in microscopic, cinnabar-red needles, melts at 156°, and has a characteristic odour. The acid appears to be oxidised by nitric acid to the corresponding disulphonic acid.
T. M. L.

Some Carbamides, Thiocarbamides, and Ethyl Carbamates of Pyridine. By RUDOLF CAMPS (*Arch. Pharm.*, 1902, **240**, 345—365).—*iso*Nicotinic acid was found to melt at 315°.

The carboxylic acids, $C_5NH_4\cdot CO_2H$, were converted into the esters $C_5NH_4\cdot CO_2Et$ by heating them on the water-bath with a mixture of equal weights of alcohol and sulphuric acid; the 4-*ester*, boiling at 218°, takes up ethyl iodide, and when the additive compound is treated with moist silver oxide it forms a silver salt from which, by treatment with hydrogen sulphide and evaporation of the filtered liquid, the *ethylbetaine* of *iso*nicotinic acid,  $C\begin{matrix}\mathrm{CH\cdot CH}\\ \mathrm{CO{-}O}\\ \mathrm{CH{:}CH}\end{matrix}NEt$, melting and decomposing at 241°, was obtained. The esters were converted into the amides $C_5NH_4\cdot CO\cdot NH_2$ by pouring concentrated ammonia over them and allowing the mixture to remain at the ordinary temperature; the 4-*amide* melts at 155° when anhydrous, at 117—120° when crystallised with water. The amides were converted into the aminopyridines, $C_5NH_4\cdot NH_2$, by treatment with a solution of bromine in aqueous potassium hydroxide; at the same time, *dibromoaminopyridines*, $C_5NH_2Br_2\cdot NH_2$, melting at 137°, 148°, and 167° in the case of the 2-, 3-, and 4-compounds respectively, were formed in small amount, and also some *bromo-2-aminopyridine*, $C_5NH_3Br\cdot NH_2$, melting at 106—107° and crystallising in slender, lustrous needles, and a *substance* melting at 126°, probably a complex carbamide derivative (compare Pollak, Abstr., 1895, i, 391), in the cases of the 2- and 3-compounds respectively. The amines condense with acetic anhydride to form the *acetylaminopyridines*, $C_5NH_4\cdot NHAc$, or "antifebrines" of the pyridine series, which melt respectively at 71°, 133°, and 150° (when anhydrous; the last at 124° when crystallised with water). The amines are all converted into hydroxypyridines (pyridones) when diazotised in cold sulphuric acid solution (compare Marckwald, Abstr., 1894, i, 381, who obtained chloropyridine only when diazotising in hydrochloric acid solution).

With ethyl chloroformate in ethereal solution, they form *ethyl pyridinecarbamates* (*urethanes*), $CO_2Et\cdot NH\cdot C_5NH_4$, melting respectively at 105°, 90°, and 129°, and sometimes also a little of the *dipyridylcarbamides*, $CO(NH\cdot C_5NH_4)_2$, which can always be obtained by the further action of the amine on the carbamate, and melt at 175°, 225°, and 208° respectively; with aniline, the 2-carbamate forms 2-*pyridylphenylcarbamide*, $\mathrm{NHPh\cdot CO\cdot NH\cdot C_5NH_4}$, crystallising in slender needles and melting at 180°. With phenylthiocarbimide, the aminopyridines condense to pyridylphenylthiocarbamides,

$$\mathrm{NHPh\cdot CS\cdot NH\cdot C_5NH_4},$$

which melt at 171°, 164°, and 148° respectively. When heated with carbon disulphide in alcoholic solution, 2-aminopyridine forms *dipyridylthiocarbamide*, $\mathrm{CS(NH\cdot C_5NH_4)_2}$, crystallising in lustrous, highly refractive, long needles or prisms, and melting at 163°, along with small quantities of *substances* melting at 147° and 85° respectively; the 4-amine forms *ethyl* 4-*pyridylthiocarbamate*, $\mathrm{OEt\cdot CS\cdot NH\cdot C_5NH_4}$, crystallising in needles and melting at 110° when anhydrous, at 92—93° when crystallised with water, together with a yellow substance, probably 4-*aminopyridine* 4-*pyridyldithiocarbamate*,

$$\mathrm{C_5NH_4\cdot NH_2,SH\cdot CS\cdot NH\cdot C_5NH_4},$$

which melts and decomposes at 152°. C. F. B.

Condensation of 2:4-Lutidine with *p*-Nitrobenzaldehyde. By R. Knick (*Ber.*, 1902, 35, 2790—2793. Compare Bialon, this vol., i, 828).—p-*Nitrophenyl*-2:4-*lutidylalkine*,

$$\mathrm{NO_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot C_5NH_3Me},$$

produced by heating 2:4-lutidine and *p*-nitrobenzaldehyde at 130—135°, crystallises from alcohol in yellow plates melting at 168—169°; the base is insoluble in water and dissolves only sparingly in the other organic solvents. The *hydrochloride* separates in fern-like crystals and melts at 242°; the *picrate* crystallises from water in golden spangles containing $1H_2O$, the anhydrous salt melts at 171°; the *benzoate*, $\mathrm{C_{21}H_{18}O_4N_2}$, forms white flakes decomposing at 214°; the *platinichloride* melts at 219°.

The preceding base yields p-*aminophenyl*-2:4-*lutidylalkine* on reduction with tin and hydrochloric acid; this melts at 130° and yields a *platinichloride* crystallising in orange-red needles and decomposing at 222°; the *mercurichloride* separates in needles and melts at 236°.

p-*Nitro*-4-*methylstilbazole*, $\mathrm{NO_2\cdot C_6H_4\cdot CH{:}CH\cdot C_5NH_3Me}$, is a bye-product in the preceding condensation; it crystallises in pale yellow, lustrous leaflets and melts at 134°; the *hydrochloride* separates in yellow needles melting at 234—235°; the *platinichloride* and *mercurichloride* melt respectively at 237° and 187° respectively; the base also yields a *dibromide*.

p-*Amino*-4-*methylstilbazole*, produced by reducing the preceding base, melts at 119° and yields a *hydrochloride* and a *dibromide*, separating in white crystals and decomposing respectively at 208° and 157°; the *platinichloride* and *mercurichloride* form yellow needles; the former darkens at 280° without melting, the latter decomposes at 176°.

G. T. M.

Reduction Products of α- and γ-Benzylpyridines. By A. E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1902, 34, 508—514).—By the reduction of 2- and 4-benzylpyridines with sodium in alcoholic solution, yields of 60—70 per cent. of the corresponding benzyl piperidines are obtained.

i-2-*Benzylpiperidine*, $CH_2Ph\cdot C_5NH_{10}$, boils at 267—268° and crystallises in needles melting at 32°; it has a faint odour resembling that of piperidine and is soluble in alcohol or ether; the *hydrochloride* forms hydrated, acicular crystals which melt at 58°, whilst the anhydrous salt melts at 137°; the *platinichloride* crystallises from water in yellow needles which melt, with incipient blackening, at 210°; the *aurichloride* separates as golden-yellow, flattened needles melting at 168—170°; the *picrate* crystallises from alcohol or acetone in short, thick prisms which melt at 156—157° and are slightly soluble also in water or benzene.

4-*Benzylpiperidine*, $CH_2Ph\cdot C_5NH_{10}$, is a liquid having a faint odour of piperidine and boiling at 279°; when strongly cooled, it yields a crystalline mass melting at 6—7°. It is soluble in alcohol or ether and has a sp. gr. 0·9972 at 20°/0°. The *hydrochloride* froms white scales melting at 172—173°; from aqueous solutions, the *platinichloride* separates in large, shining plates melting at 197°, the *aurichloride* in plates melting at 145—146°, and the *picrate* in long, thin, shining prisms melting at 184°.

4-*Benzyltetrahydropyridine* (4-*benzylpiperidine*), $CH_2Ph\cdot C_5NH_8$, which is also obtained from the reduction of 4-benzylpyridine, is a viscous liquid having an odour resembling that of sperm oil and boiling at 280—282°; its sp. gr. is 1·018 at 20°/0°. Its *picrate* separates from alcohol in thick prisms melting at 129—131°; the *platinichloride* separates from water in yellow prisms melting at 193—195°.

The mother liquor from the reduction of the 2-compound also yields a small quantity of a liquid boiling at 270—272°, but there was not sufficient to allow of its investigation. T. H. P.

Nitro- and Amino-stilbazoles. By Ernst Schmidt (*Arch. Pharm.*, 1902, **240**, 390).—The meta-compounds lately described (Feist, this vol., i, 642) had been obtained already by Schuftan (Abstr., 1890, 1438). C. F. B.

Action of *p*-Tolualdehyde on 2-Picoline and 2-Methyl-6-phenylpyridine. By Wolfgang Dierig (*Ber.*, 1902, **35**, 2774—2779).—p-*Methyl-2-stilbazole*, $C_5NH_4\cdot CH{:}CH\cdot C_6H_4Me$, produced by condensing 2-picoline and *p*-tolualdehyde with zinc chloride at 180°, separates from dilute alcohol in colourless, felted crystals and melts at 82°; it is insoluble in water, but dissolves in the ordinary organic solvents and forms a *hydrochloride*, $C_{14}H_{13}N,HCl,H_2O$, crystallising from water or alcohol in pale yellow needles sintering at 170° and melting at 190—191°. The *platinichloride*, $(C_{14}H_{13}N)_2,H_2PtCl_6,H_2O$, decomposes at 194—195°; the *aurichloride* crystallises in flattened, red needles decomposing at 180—181°; the *mercurichloride* forms yellow needles blackening at 219° and decomposing at 225°; the *picrate* separates in yellow needles and melts at 193—194°. A bromine *additive product*, $C_{14}H_{13}NBr_2,HBr$, is obtained in the form of its hydrobromide by mixing bromine and the base in carbon disulphide solution; it decomposes at 170°.

p-*Methyldihydro-2-stilbazole*, $C_5NH_4\cdot CH_2\cdot CH_2\cdot C_6H_4Me$, prepared by heating the preceding base with concentrated hydriodic acid at 140—150°, is a colourless oil boiling at 294—296° under the ordinary pressure; it has a neutral reaction and is darkened by exposure to light. The platinichloride and aurichloride crystallise in yellow needles and melt respectively at 180° and 138—140°.

p-*Methyl-2-stilbazoline*, $C_{14}H_{21}N$, resulting from the action of sodium and alcohol on *p*-methyl-2-stilbazole, is an oil boiling at 145—148° under 11 mm. pressure and having a characteristic, disagreeable odour. The *platinichloride*, *aurichloride*, and *picrate* crystallise in yellow needles melting respectively at 182°, 136°, and 125°.

p-*Tolyl-2-picolylalkine*, $C_5NH_4\cdot CH_2\cdot CH(OH)\cdot C_6H_4Me$, resulting from the action of *p*-tolualdehyde on 2-picoline at 140°, crystallises from alcohol in lustrous needles melting at 93°; the *platinichloride* is a red, crystalline substance sintering at 140° and melting at 150°; the *aurichloride* forms golden-yellow needles soluble in water or alcohol, but not in ether; it melts at 131°.

6-*Phenyl*-p-*methyl-2-stilbazole*, $C_5NH_3Ph\cdot CH\!:\!CH\cdot C_6H_4Me$, prepared by condensing 6-phenyl-2-methylpyridine and *p*-tolualdehyde with zinc chloride at 180—190°, crystallises from alcohol in needles and from ether in thick spicules; it melts at 113°. The *hydrochloride*, $C_{20}H_{17}N,HCl,H_2O$, separates in yellow needles from water or alcohol; it sinters at 195° and melts at 202°. The *platinichloride*,

$$(C_{20}H_{17}N)_2,H_2PtCl_6,H_2O,$$

the *aurichloride*, and the *mercurichloride* crystallise in needles, and the last of these salts melts at 183°. The *picrate* crystallises with $3H_2O$ and melts at 196°; the bromine *additive* compound separates from alcohol in transparent leaflets and melts at 173°.

6-*Phenyl*-p-*methyl-2-stilbazoline*, produced by reducing the preceding base with sodium and alcohol, is a pale yellow oil having a disagreeable odour and boiling at 245° under 20 mm. pressure which solidifies to a glistening mass in a freezing mixture. The *hydrochloride* separates in white crystals soluble in water or alcohol; it sinters at 230° and melts at 250°; the *picrate* crystallises in needles sintering at 180° and melting at 197°. G. T. M.

Action of Aldehydes on 6-Phenyl-2-methylpyridine. By Otto Ollendorff (*Ber.*, 1902, **35**, 2782—2786. Compare Abstr., 1901, i, 165; this vol., i, 234 and 818).—6-*Phenyl-2-picolyl*-p-*nitrophenylalkine*, $C_5NH_3Ph\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot NO_2$, produced by condensing 6-phenyl-2-methylpyridine, *p*-nitrobenzaldehyde, and a small quantity of water at 140°, crystallises from alcohol in white needles and melts at 112°; the *hydrochloride*, $C_{19}H_{16}O_3N_2,HCl,H_2O$, separates in tabular crystals from its alcoholic solution on adding hydrochloric acid; it melts at 126°. The *platinichloride* forms yellow prisms and melts at 212°.

6-*Phenyl*-2-p-*nitrostilbazole*, $C_5NH_3Ph\cdot CH\!:\!CH\cdot C_6H_4\cdot NO_2$ crystallises from alcohol in lustrous plates melting at 142°; it is obtained in small quantity by condensing 6-phenyl-2-methylpyridine and *p*-nitrobenzaldehyde at 150° in the presence of zinc chloride. The *hydrochloride* crystallises in white needles and melts at 135°.

6-*Phenyl*-2-p-*methoxystilbazole*, $C_5NH_3Ph\cdot CH{:}CH\cdot C_6H_4\cdot OMe$, prepared in a similar manner from the substituted pyridine base and anisaldehyde, crystallises in white needles and melts at 129°; the *hydrochloride* separates in yellow needles melting at 200°, the hydrobromide is obtained in fan-shaped aggregates; the *double thallic* salt,

$$TlCl_3,(C_{20}H_{17}ON,HCl)_2$$

(compare Renz, this vol., i, 822), crystallises from dilute alcohol in yellow leaflets melting at 98°; the *platinichloride* crystallises in prisms melting at 245° and the *mercurichloride* in yellow needles melting at 221°.

The preceding stilbazole derivative, when reduced with sodium and alcohol, yields an oily *base* which is characterised by its *hydrochloride*, $C_{20}H_{25}ON,HCl$, a substance crystallising in needles melting at 229°.

2-ω-*Trichloro*-β-*hydroxypropyl*-6-*phenylpyridine*,

$$C_5NH_3Ph\cdot CH_2\cdot CH(OH)\cdot CCl_3,$$

produced by heating 6-phenyl-2-methylpyridine with chloral on the water-bath, crystallises in triclinic plates melting at 65° and containing $1\frac{1}{2}H_2O$; its *platinichloride*, $(C_{14}H_{12}ONCl_3),H_2PtCl_6,2H_2O$, crystallises in red needles and melts at 201°.

6-*Phenyl*-2-*pyridylacrylic acid*, $C_5NH_3Ph\cdot CH{:}CH\cdot CO_2H$, results from the action of alcoholic potassium hydroxide on the preceding base and is isolated in the form of its hydrochloride; the *platinichloride*, $(C_{14}H_{11}O_2N)_2,H_2PtCl_6$, crystallises from alcohol in yellow leaflets and melts at 204°.

G. T. M.

Action of Anisaldehyde on Quinaldine, 2-Picoline, and 2-Methyl-5-ethylpyridine. By O. Bialon (*Ber.*, 1902, **35**, 2786–2790. Compare preceding abstracts).—*Anisylidenequinaldine*,

$$OMe\cdot C_6H_4\cdot CH{:}CH\cdot C_9NH_6,$$

produced by condensing quinaldine and anisaldehyde at 180° in the presence of zinc chloride, crystallises from alcohol in white, lustrous leaflets melting at 126°; the *hydrochloride* separates from water in yellow needles and melts at 208°; the *platinichloride* is a yellow, insoluble substance melting at 254°; the *aurichloride* is also yellow, crystallises from dilute hydrochloric acid and melts at 199°; the *picrate* crystallises from acetone in yellow needles. When reduced with sodium and alcohol, the preceding base gives rise to p-*methoxybenzyltetrahydroquinaldine*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_9NH_{10}$, a secondary amine crystallising from alcohol in white, silky needles melting at 71°; the *benzoyl* derivative, prepared by the Schotten-Baumann reaction, crystallises in white needles and melts at 97°; the *hydrochloride* separates in yellow, feathery crystals and melts at 218°, the *aurichloride* and *platinichloride* are unstable.

p-*Methoxy*-2-*stilbazole*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot C_5NH_4$, obtained in a poor yield by heating α-picoline and anisaldehyde at 180—190° for 36 hours in the presence of zinc chloride, crystallises from alcohol in lustrous, silvery leaflets melting at 75°; the *hydrochloride* separates from hot water in yellow needles and melts at 200—201°; the *auri-*

chloride and *platinichloride* melt respectively at 178° and 225° (compare Schuftan, Abstr., 1889, 1437). On reduction with sodium and alcohol, the preceding base yields an oily *amine*, the hydrochloride of which crystallises in white needles and melts at 173°; the double salts with platinum, gold, and mercury are unstable, oily products.

p-*Methoxy-5-ethyl-2-stilbazole*, $OMe\cdot C_6H_4\cdot CH\colon CH\cdot C_5NH_3Et$, resulting from the interaction of 2-methyl-5-ethylpyridine and anisaldehyde, was only isolated in the form of *aurichloride* and platinichloride, these salts melting respectively at 137° and 201°; the latter crystallises in yellow needles. G. T. M.

Compounds of Quinoline and *iso*Quinoline with Cupric and Cuprous Thiocyanates. By Franz M. Litterscheid (*Arch. Pharm.*, 1902, **240**, 386—390. Compare Abstr., 1901, i, 635; this vol., i, 308).

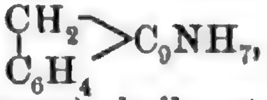
—Quinoline and *iso*quinoline unite with dry cupric thiocyanate, forming green *substances* of the composition $Cu(C_9NH_7\cdot CNS)_2$.

With cuprous thiocyanate, they unite to form golden-yellow *crystals* with the composition $Cu_2(C_9NH_7\cdot CNS)_2,2C_9NH_7$. When dried at 100°, these leave, first, lemon-yellow *substances* with the composition $Cu_2(C_9NH_7\cdot CNS)_2$, and finally cuprous thiocyanate.

With cuprosocupric thiocyanate, the golden-yellow crystals mentioned above were obtained. C. F. B.

Preparation and Properties of some Quinoline Bases of Fluorene and Fluorenone. II. By Otto Diels and Otto Staehlin (*Ber.*, 1902, **35**, 3275—3284. Compare Abstr., 1901, i, 521).

—2-Aminofluorene (*loc. cit.*), when boiled with glycerol, arsenic acid, and concentrated sulphuric acid, gives *fluorenequinoline*,



$\left.\begin{matrix}CH_2\\ C_6H_4\end{matrix}\right>C_9NH_7$,

which crystallises in white plates, melts at 134·5° (corr.), boils at 390—400°, and is almost insoluble in water or cold alcohol, but soluble in hot alcohol, methyl alcohol, benzene, or acetone; it is only when fresh that it dissolves in ether, but it easily dissolves in chloroform. The *hydrochloride* forms yellow needles containing $2H_2O$ and melting at 110°, or when anhydrous at 241° (corr.). The salts are in general fairly insoluble. The *methiodide*, $C_{17}H_{14}NI,H_2O$, when anhydrous, decomposes at 241° (corr.) without melting. When reduced with zinc and hydrochloric acid, the quinoline base gives *fluorenetetrahydroquinoline*, $C_{16}H_{15}N$, which forms white needles, melts at 143° (corr.), is insoluble in cold water, slightly soluble in alcohol to a blue fluorescent solution, and easily so in ether, acetone, benzene, or chloroform. Its hydrochloride crystallises well, as do also the sulphate, nitrate, and platinichloride. With oxidising agents, the tetrahydro-compound gives an indigo-blue coloration, which becomes violet, then brown; it reduces an ammoniacal silver solution. Nitrous acid converts it into a nitroso-compound of the formula $C_{16}H_{14}ON_2$. This nitrosoamine melts at 162° (corr.) and is insoluble in water, but soluble in chloroform, acetone, or benzene, or in concentrated sulphuric acid to a greenish solution; it responds to the Liebermann nitroso-reaction. The *phenylcarbimide* of the tetrahydro-base, $C_{23}H_{20}ON_2$, melts at 208°.

Fluorenequinoline, when oxidised with sodium dichromate and acetic acid, gives a new base which forms yellow crystals, melts at 191° (corr.), and has the formula $C_{16}H_9ON$. This is insoluble in cold water or alcohol, but easily soluble in benzene or chloroform. Its *hydrochloride*, *sulphate*, and *nitrate* have been prepared.

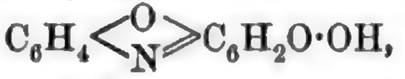
2-Aminofluorenone, when boiled with glycerol, arsenic acid, and concentrated sulphuric acid, gives *fluorenonequinoline*, which crystallises in yellow needles and melts at 188°. The *methiodide*, $C_{17}H_{12}ONI,H_2O$, is insoluble in all organic solvents and decomposes when heated at 240°.

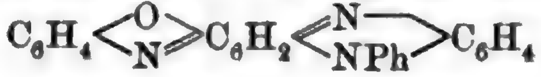
When fluorenonequinoline is fused with potassium hydroxide, the potassium salt of a carboxylic acid of the formula $C_{15}H_{10}N\cdot CO_2H$ is obtained. The free acid can be crystallised from hot alcohol, melts at 264—265° (corr.), and is insoluble in water, ether, chloroform, or acetone, but is soluble in solutions of acids or bases. J. McC.

Some Ammonium Compounds. X. Hydroxyphenylmethyldihydroacridine. By Herman Decker, Th. Hock, and C. Djiwonsky (*Ber.*, 1902, **35**, 3068—3079. Compare Abstr., 1893, i, 115; this vol., i, 691).—The *methyl ether* of 5-hydroxy-5-phenyl-10-methyl-5:10-dihydroacridine is formed when the carbinol base is boiled with methyl alcohol. It forms colourless needles which melt at 152—153°, and become red. The corresponding iso*butyl ether* also forms colourless crystals which melt at 108·5°. Halogens act on hydroxyphenylmethyldihydroacridine, and with iodine the *di-iodide* of *phenylacridine methiodide* is produced, which crystallises from chloroform in dark, six-sided plates and melts at 148—150°. With excess of iodine, a polyiodide is formed.

The action of methyl iodide on the carbinol base is to reproduce phenylacridine methiodide.

From a consideration of the work of Werner, Kehrmann, and others, the authors deduce support for the theories which Decker has already advanced for the constitution and mode of formation of these ammonium compounds. J. McC.

Oxidation Products of *o*-Aminophenol. By Emil Diepolder (*Ber.*, 1902, **35**, 2816—2822).—When *o*-aminophenol hydrochloride is oxidised with potassium ferricyanide or ferric chloride, a mixture of triphenodioxazine and 3-hydroxybenzeneazoxindone is obtained. 3-*Hydroxybenzeneazoxindone*,  $C_6H_4{<}\substack{O\\N}{>}C_6H_2O\cdot OH$, which is the tautomeric form of phenoxazine-2:3-quinone, crystallises from xylene in beautiful, brown needles with a blue iridescence, blackens at 240—250°, and decomposes at 278°; it is soluble in ammonia and when treated with sodium hydroxide yields *o*-aminophenol and dihydroxyquinone. The *acetyl* derivative crystallises in clusters of golden, lustrous leaflets and melts at 225—226°. An insoluble byeproduct which decomposed at 268°, obtained in the above oxidation, was proved to be a double *compound* of 3-hydroxybenzeneazoxindone and 3-aminobenzeneazoxindone. 7-*Phenyltriphenazineoxazine*,



$$C_6H_4{<}\substack{O\\N}{>}C_6H_2{<}\substack{N\text{——}\\NPh}{>}C_6H_4$$

(Abstr., 1898, i, 93) crystallises from nitrobenzene and is identical with the compound wrongly described as N-methyltriphenazinoxazinecarbazole (Abstr., 1901, i, 618).

A red coloration with ferric chloride, which is converted into blue or green with reducing agents such as stannous chloride, seems to be characteristic for those *o*-aminophenols which have two free para-positions, and not more than one alkyl in the amino-group.

R. H. P.

Aminohydroxydiphenylamine and Analogous Compounds. By ROBERT GNEHM [with H. BOTS and G. WEBER] (*Ber.*, 1902, **35**, 3085—3088).—By the condensation of dimethyl-*p*-phenylenediamine with quinol or by the reduction of phenol-blue, *dimethyl*-p-*amino*-p-*hydroxydiphenylamine* is obtained in the form of white needles which melt at 161°. Its *diacetyl* derivative melts at 131° and its *dibenzoyl* derivative at 210°. When treated with concentrated nitric acid, the diacetyl compound loses the acetyl groups and a *tetranitro*-compound melting at 228° is formed. With methyl iodide or ethyl iodide, direct addition takes place and well crystallised products melting at 218° and 206° respectively are obtained.

When resorcinol is used in place of quinol, *dimethyl*-p-*amino*-m-*hydroxydiphenylamine* is formed; this is easily soluble in the common organic solvents or in hot water and melts at 99°. It forms a *diacetyl* compound which melts at 101° and a *dibenzoyl* derivative which melts at 112°. With nitrous acid, it gives a *nitrosoamine*, which separates from dilute alcohol in brownish needles and melts at 125·5°.

By the reduction of indamine, *dimethyl*-p-*diaminodiphenylamine* is formed. It is soluble in hot water and melts at 116°.

2-p-*Dimethylanilino-7-hydroxynaphthalene*, $NMe_2\cdot C_6H_4\cdot NH\cdot C_{10}H_6\cdot OH$, is produced from dimethyl-*p*-phenylenediamine and 2 : 7-dihydroxynaphthalene; it crystallises in white plates and melts at 126—127°.

J. McC.

Benzylidenehydrazine. By THEODOR CURTIUS and H. FRANZEN (*Ber.*, 1902, **35**, 3234—3239).—Benzylidenehydrazine, $CHPh\colon N\cdot NH_2$ (Curtius and Pflug, Abstr., 1892, 456), is best prepared by the action of hydrazine on benzaldazine, $CHPh\colon N\cdot N\colon CHPh$. The *picrate*, $CHPh\colon N\cdot NH_2,C_6H_2(NO_2)_3\cdot OH$, separates as a thick, yellow precipitate and is sparingly soluble in all solvents. It condenses with phenylthiocarbimide to form benzylidenephenylthiosemicarbazide, $CHPh\colon N\cdot NH\cdot CS\cdot NHPh$ (Pulvermacher, Abstr., 1894, i, 304), and with acetic anhydride gives acetylbenzylidenehydrazine (Curtius and Schäfer, Abstr., 1895, i, 263), whilst ethyl bromide converts it into hydrazine hydrobromide and benzaldazine.

o-Hydroxybenzylidenehydrazine (Cajar, Abstr., 1899, i, 146) can be prepared in a similar manner from the azine; the *picrate* forms a yellow, slightly soluble, crystalline powder. o-*Hydroxybenzylidenephenylthiosemicarbazide*, $OH\cdot C_6H_4\cdot CH\colon N\cdot NH\cdot CS\cdot NHPh$, separates from alcohol in white flakes or needles.

2 : 4 : 5-*Trimethylbenzylidenehydrazine*, $C_6H_2Me_3\cdot CH\colon N\cdot NH_2$, from 2 : 4 : 5-trimethylbenzaldazine (Graf, *Diss.*, Heidelberg, 1899), boils

at 165—166° under 14 mm. pressure, solidifies in the receiver, melts at 70°, and dissolves readily in organic solvents; the *picrate* is a yellow, slightly soluble, crystalline powder and melts at 170—171°; 2 : 4 : 5-*trimethylbenzylidenebenzylidenehydrazine*,

$$C_6H_2Me_3\cdot CH{:}N\cdot N{:}CHPh,$$

separates from alcohol in yellow needles; the *o*-hydroxybenzylidenehydrazine, $C_6H_2Me_3\cdot CH{:}N\cdot N{:}CH\cdot C_6H_4\cdot OH$, crystallises from alcohol in yellow needles.

p-*Methylbenzylidenehydrazine*, $C_6H_4Me\cdot CH{:}N\cdot NH_2$, is a white, crystalline substance, boils at 148° under 12 mm. pressure, and melts at 56°; the *picrate* is a yellow, crystalline powder and melts at 175—176°. p-*Methylbenzylidenebenzylidenehydrazine*, $C_6H_4Me\cdot CH{:}N\cdot N{:}CHPh$, separates from alcohol in yellow needles.

m-*Chlorobenzylidenehydrazine*, $C_6H_4Cl\cdot CH{:}N\cdot NH_2$, is a white, crystalline substance and boils at 163—164° under 20 mm. pressure; the *benzylidenehydrazine*, $C_6H_4Cl\cdot CH{:}N\cdot N{:}CHPh$, separates from alcohol in yellow needles. T. M. L.

Preparation of Hydrazides from Diammonium Salts. By THEODOR CURTIUS and H. FRANZEN (*Ber.*, 1902, **35**, 3239—3241).—Hydrazides can be prepared in good yield by directly heating the hydrazine salts of the acids; the preparation of acetyl-, propionyl-, lactyl-, and benzoyl-hydrazines by this method is described.

Hydrazine p-*bromobenzoate*, $C_6H_4Br\cdot CO_2H,N_2H_4$, separates from alcohol in colourless needles, softens at 165°, melts at 170°, and dissolves readily in alcohol or water. When heated, it is converted into *di*-p-*bromobenzoylhydrazine*, $N_2H_2(CO\cdot C_6H_4Br)_2$, which crystallises from alcohol in minute, colourless needles and melts at 280°; *p*-bromobenzoylhydrazine was not produced.

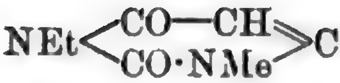
Hydrazine p-*toluate*, $C_6H_4Me\cdot CO_2H,N_2H_4$, forms colourless, soluble needles, and when heated is converted into a mixture of *p*-toluoylhydrazine and *p*-ditoluoylhydrazine. T. M. L.

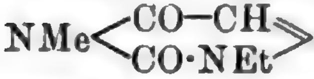
Constitution of the Alkyl Derivatives of Methyluracil and δ-Methyluric Acid. By ROBERT BEHREND and RICHARD THURM (*Annalen*, 1902, **323**, 160—178. Compare Abstr., 1900, i, 63).—The dimethyluracils are most conveniently prepared by methylating 4-methyluracil with less than the calculated quantities of methyl iodide and potassium hydroxide; under these conditions, the mixture of dimethyl derivatives contains 60 per cent. of the β-compound and 40 per cent. of the α-isomeride, the formation of trimethyluracil being reduced to a minimum.

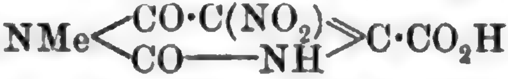
Both these compounds, on further methylation, yield the same trimethyl derivative, namely, 1 : 3 : 4-*trimethyluracil*; this compound separates in rhombic crystals melting at 110—112°; like the monomethyl compound, it may be sublimed without decomposition.

The two dimethyl derivatives, on oxidation, give rise to the same methyloxaluric acid, the products of the two reactions being shown to be crystallographically identical. The following results indicate that α-dimethyluracil is 3 : 4-*dimethyl*-2 : 6-*dioxypyrimidine*, whilst its β-isomeride is 1 : 4-*dimethyl*-2 : 6-*dioxypyrimidine*.

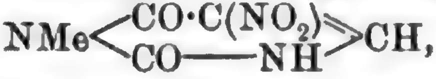
3 : 4-*Dimethyl*-1-*ethyluracil* (3 : 4-*dimethyl*-1-*ethyl*-2 : 6-*dioxypyrimidine*,

 $\mathrm{NEt}<\begin{array}{l}\mathrm{CO{-}CH}\\ \mathrm{CO{\cdot}NMe}\end{array}>\mathrm{CMe}$, produced by ethylating *a*-dimethyluracil with ethyl iodide or bromide, crystallises from benzene in lustrous leaflets melting at 112—114°.

1:4-*Dimethyl*-3-*ethyluracil* (1:4-*dimethyl*-3-*ethyl*-2:6-*dioxypyrimidine*),  $\mathrm{NMe}<\begin{array}{l}\mathrm{CO{-}CH}\\ \mathrm{CO{\cdot}NEt}\end{array}>\mathrm{CMe}$, prepared in a similar manner from *β*-dimethyluracil, crystallises from alcohol in prisms and melts at 110—112°.

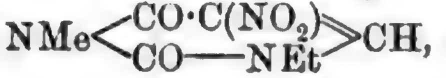
1-*Methyl*-2 : 6-*dioxy*-5-*nitropyrimidine*-4-*carboxylic acid* (*β-methylnitrouracilcarboxylic acid*),  $\mathrm{NMe}<\begin{array}{l}\mathrm{CO{\cdot}C(NO_2)}\\ \mathrm{CO{-\!-}NH}\end{array}>\mathrm{C{\cdot}CO_2H}$, is produced by oxidising *β*-dimethyluracil with a mixture of sulphuric and nitric acids, the latter being saturated with nitrous fumes; it separates from water in light yellow crystals containing $2H_2O$. The water of crystallisation is evolved at 100°, and carbon dioxide is eliminated at 140—150°. The *double* salt, $2C_6H_4O_6N_3K,KNO_3,2H_2O$, separates in feathery crystals when the crude product of oxidation is neutralised with potassium hydroxide. The *simple* salt, $C_6H_4O_6N_3K,H_2O$, separates in yellow crystals from an aqueous solution of the preceding compound. The crude acid also contains a less soluble *substance*, $C_6H_4O_5N_4$, which dissolves in hot water, yielding an acid solution which develops an intense yellow coloration with the alkalis.

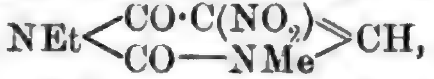
1-*Methyl*-2 : 6-*dioxy*-5-*nitropyrimidine* (*β-methylnitrouracil*),



$$\mathrm{NMe}<\begin{array}{l}\mathrm{CO{\cdot}C(NO_2)}\\ \mathrm{CO{-\!-}NH}\end{array}>\mathrm{CH},$$

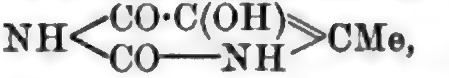
produced on heating the preceding acid, crystallises from water in colourless needles and melts at 263° with partial decomposition; its potassium derivative is obtained by heating the potassium salt of the preceding acid.

1-*Methyl*-3-*ethyl*-2 : 6-*dioxy*-5-*nitropyrimidine* (1-*methyl*-3-*ethylnitrouracil*),  $\mathrm{NMe}<\begin{array}{l}\mathrm{CO{\cdot}C(NO_2)}\\ \mathrm{CO{-\!-}NEt}\end{array}>\mathrm{CH}$, obtained by heating the silver derivative of the preceding compound with ethyl iodide at 100°, crystallises from water in prismatic needles and melts at 105—106°; this substance is identical with the product formed by successively ethylating and methylating the potassium derivative of nitrouracil.

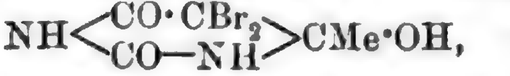
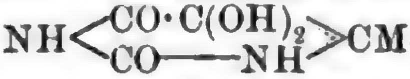
3-*Methyl*-1-*ethyl*-2 : 6-*dioxy*-5-*nitropyrimidine* (3-*methyl*-1-*ethylnitrouracil*),  $\mathrm{NEt}<\begin{array}{l}\mathrm{CO{\cdot}C(NO_2)}\\ \mathrm{CO{-}NMe}\end{array}>\mathrm{CH}$, prepared from *a*-methylnitrouracil, crystallises from water in needles melting at 124°; it is decomposed, on prolonged heating, in aqueous or alcoholic solution; Lehmann, who first obtained the two preceding dialkylated nitrouracils, gave the melting point of the former as 70—73° and that of the latter as 106—109° (compare Abstr., 1890, 33).

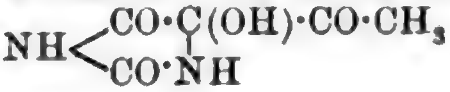
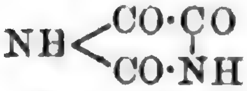
a-Dimethyluracil can be successively converted into 3-methylnitrouracil, 3-methyl*iso*barbituric acid, 3-methyl*iso*dialuric acid, and δ-methyluric acid. If, therefore, the original substance is 3 : 4-dimethyl-2 : 6-dioxypyrimidine, the final product must contain its methyl group in position 3 of the pyrimidine ring, and this cycle of changes supplies confirmatory evidence in support of Fischer's view that the acid in question is 3-methyluric acid. G. T. M.

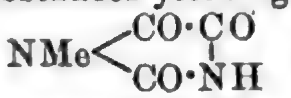
Oxidation of Methyluracil. By ROBERT BEHREND and RICHARD GRÜNEWALD (*Annalen*, 1902, **323**, 178—204. Compare preceding abstract).—When methyluracil is oxidised with an amount of potassium permanganate equivalent to three atoms of oxygen, acetylcarbamide and oxaluric acid are produced, the relative proportion of these substances depending on the temperature; in the cold, the former compound is the chief product, at the boiling point, the latter predominates, whilst the two are formed in approximately equal amounts at 40—50°. This result is obtained, however, only in alkaline solutions; if the mixture becomes neutral or acid, the proportion of acetylcarbamide increases and predominates even at high temperatures.

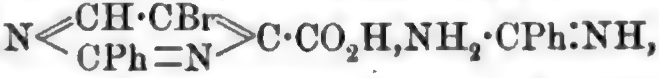
3-*Hydroxy*-4-*methyluracil*,  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\cdot C(OH)}\\ \mathrm{CO{-}{-}NH}\end{array}>\mathrm{CMe}$, is produced when 4-methyluracil is oxidised with one atomic proportion of oxygen by means of permanganate solution, the maximum yield being obtained at 20—40°, when the solution is rendered neutral by the addition of an equivalent amount of acetic acid. The substance is sparingly soluble in water or alcohol, but readily dissolves in alkaline or ammoniacal solutions; it forms prismatic, anisotropic crystals having either pyramidal or truncated ends; with neutral ferric chloride, it develops an intense blue coloration which disappears after a time, or more rapidly on warming or treating with acids or alkalis. The compound was not obtained in a state of purity, the percentage of carbon being somewhat too high.

3-*Acetoxy*-4-*methyluracil*, produced by treating the preceding substance with acetic anhydride, crystallises from water in felted needles decomposing at 238—241°; it regenerates the hydroxy-compound by alkaline hydrolysis. 3-Hydroxy-4-methyluracil, on further oxidation, gives rise to acetylcarbamide and oxaluric acid.

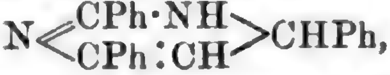
Although a compound intermediate between 3-hydroxy-4-methyluracil and its oxidation products could not be isolated, yet the soluble product, obtained by treating 3 : 3-dibromo-4-hydroxy-4-methyluracil,  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\cdot CBr_2}\\ \mathrm{CO{-}NH}\end{array}>\mathrm{CMe\cdot OH}$, with potassium hydroxide solution, appears to contain such a substance, namely, 3 : 3 : 4-*trihydroxy*-4-*methyldihydrouracil*,  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\cdot C(OH)_2}\\ \mathrm{CO{-}{-}NH}\end{array}>\mathrm{CMe\cdot OH}$, for on reduction it yields 3-hydroxy-4-methyluracil, whilst on oxidation acetylcarbamide and oxaluric acid are produced. Acetylallanturic acid is probably an intermediate product of the latter process, but it has not been isolated.

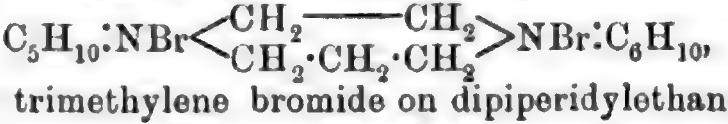
This supposition derives support from the fact that in acid or neutral solutions oxidation by chromic or permanganic acid leads to the formation of parabanic acid, a substance which should readily result from the hypothetical compound,  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\cdot C(OH)\cdot CO\cdot CH_3}\\ \mathrm{CO\cdot NH}\end{array}$ + O =  $\mathrm{NH}<\begin{array}{l}\mathrm{CO\cdot CO}\\ \mathrm{CO\cdot NH}\end{array}$ + $\mathrm{CH_3\cdot CO_2H}$.

The production of the same methyloxaluric acid from α- and β-dimethyluracils may be explained by supposing that the oxidation follows a course similar to that just indicated, the two isomerides giving rise successively to methyl derivatives of trihydroxymethyldihydrouracil and acetylallanturic acid, the latter substances yielding, by further oxidation, the same methylparabanic acid,  $NMe\Big<\begin{matrix}CO\cdot CO\\ CO\cdot NH\end{matrix}$; from which methyloxaluric acid is finally obtained. G. T. M.

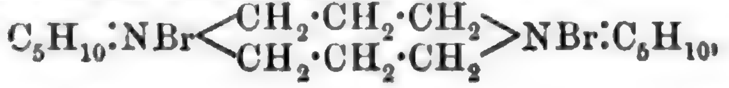
Action of Mucobromic and Mucochloric Acids on Benzamidine. By FRANZ KUNCKELL and LEO ZUMBUSCH (*Ber.*, 1902, **35**, 3164—3168. Compare Abstr., 1901, i, 759).—*Benzamidine* 5-*bromo*-2-*phenylpyrimidine*-6-*carboxylate*,  $N\Big<\begin{matrix}CH\cdot CBr\\ CPh=N\end{matrix}\Big>C\cdot CO_2H,NH_2\cdot CPh{:}NH$, is obtained when a chloroform solution of mucobromic acid is left in contact with an excess of α-benzamidine for some time, or more readily when the mixture is warmed. It is sparingly soluble in water and crystallises in colourless needles melting at 228°. The *acid* crystallises in needles, melts at 159°, and yields a *barium* salt, $C_{22}H_{12}O_4N_4Br_2Ba$, crystallising in long, colourless needles.

Bromine converts the acid into a *compound*, $C_{11}H_6O_2N_2Br_2$, and ammonia into 5-*amino*-2-*phenylpyrimidine*-6-*carboxylic acid* melting at 196°. The *hydrochloride* melts at 183°. When heated at 165—170°, the acid readily loses carbon dioxide and yields 5-*bromo*-2-*phenylpyrimidine*, melting at 104°. Mucochloric acid and benzamidine yield *benzamidine* 5-*chloro*-2-*phenylpyrimidine*-6-*carboxylate*, melting at 230—231°; the *acid* melts at 164° and the *barium* salt crystallises in long needles. 5-Chloro-2-phenylpyrimidine melts at 96°. J. J. S.

Action of Benzamidine on β-Bromo-ω-benzylacetophenone. By FRANZ KUNCKELL and O. SARFERT (*Ber.*, 1902, **35**, 3169).—2 : 4 : 6-*Triphenyl*-3 : 4-*dihydropyrimidine*,  $N\Big<\begin{matrix}CPh\cdot NH\\ CPh{:}CH\end{matrix}\Big>CHPh$, is obtained when a chloroform solution of benzamidine is warmed with β-bromo-ω-benzylacetophenone (Rupe and Schneider, Abstr., 1895, i, 361); it melts at 186—187°, is readily soluble in chloroform, alcohol, or ether, and as a feeble base combines with hydrogen chloride in the absence of water. J. J. S.

Cyclic Diammonium Compounds. By MAX SCHOLTZ (*Ber.*, 1902, **35**, 3047—3055).—The stability of cyclic compounds containing nitrogen in the ring is discussed, and the author has prepared the following compounds containing two nitrogen atoms from dipiperidylethane and dipiperidylpropane by the action of methylene iodide, ethylene bromide, trimethylene bromide, and *o*-, *m*-, and *p*-xylylene bromides. With the exception of methylene iodide, these dihalogen compounds give diammonium derivatives, as has been proved by the analysis of the platinichlorides and aurichlorides. *Ethylenetrimethylenedipiperidylium bromide*,  $C_5H_{10}{:}NBr\Big<\begin{matrix}CH_2\text{——}CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\Big>NBr{:}C_5H_{10}$, obtained by the action of trimethylene bromide on dipiperidylethane, is easily soluble in water and crystallises in rhombic plates.

Ditrimethylenedipiperidylium bromide,



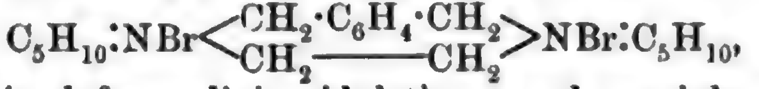
$$C_5H_{10}{:}NBr\Big<\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\Big>NBr{:}C_5H_{10},$$

obtained from dipiperidylpropane and trimethylene bromide at the ordinary temperature as a flaky mass, volatilises at 100°. The *platinichloride*, $C_{16}H_{30}N_2,H_2PtCl_6$, melts at 259°, and the *aurichloride*,

$$C_{16}H_{30}N_2,2HAuCl_4,$$

at 214°.

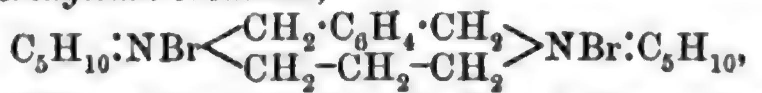
Ethylene-o-xylylenedipiperidylium bromide,



$$C_5H_{10}{:}NBr<\begin{matrix}CH_2\cdot C_6H_4\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}>NBr{:}C_5H_{10},$$

which is obtained from dipiperidylethane and *o*-xylylene bromide in chloroform solution, can be separated from alcoholic solution by means of ether as a hygroscopic, crystalline powder. The *platinichloride* does not melt but decomposes at 300°; the *aurichloride* melts at 243°. The corresponding meta- and para-compounds are similarly obtained. The *platinichloride* of the meta-compound melts at 262°, the *aurichloride* at 182°; the *platinichloride* of the para-compound melts at 235°, the *aurichloride* at 210°.

From dipiperidylpropane and the xylylene bromides, *trimethylene-xylylenedipiperidylium bromides*,



$$C_5H_{10}{:}NBr<\begin{matrix}CH_2\cdot C_6H_4\cdot CH_2\\ CH_2-CH_2-CH_2\end{matrix}>NBr{:}C_5H_{10},$$

are formed. The *platinichloride* of the ortho-compound melts at 242—243°, and the *aurichloride* at 141°. The *platinichloride* of the para-compound melts at 252°, and the *aurichloride* becomes dark at 140° and melts at 200°.

By the action of methylene iodide on dipiperidylethane and dipiperidylpropane, two mols. of the iodide combine with one mol. of the base with formation of *dipiperidylethanebisiodomethyl iodide*,

$$[C_5H_{10}{:}NI(CH_2I)]_2C_2H_4,$$

and *dipiperidylpropanebisiodomethyl iodide*,

$$[C_5H_{10}{:}NI(CH_2I)\cdot CH_2]_2CH_2;$$

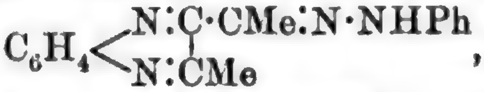
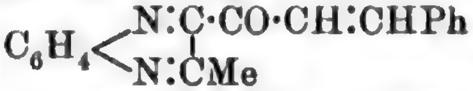
the former crystallises in yellow plates, is insoluble in ether, and melts at 182°; the latter forms yellow crystals, melts at 195—196°, and is sparingly soluble in alcohol or water, and insoluble in ether.

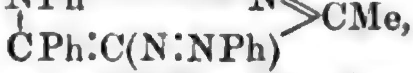
J. McC.

Synthesis of Xanthine Derivatives by means of *p*-Nitrophenol.

By WALTHER BORSCHE (*Chem. Centr.*, 1902, ii, 284—285; from *Nachr. k. Ges. Wiss. Göttingen*, 1902, 141—145. Compare Störmer, Abstr., 1901, i, 726).—*Dinitrodihydroxymethylxanthine*, $C_{15}H_{12}O_7N_2$, obtained in almost theoretical quantity by the action of formaldehyde on *p*-nitrophenol in presence of dilute sulphuric acid at 40°, separates from alcohol in colourless crystals, melts at 148°, is insoluble in alkalis, and when warmed with nitric acid yields picric acid. By the action of potassium permanganate and chromic acid, nitrosalicylic acid and 2 : 7-*dinitroxanthine*-4 : 5-*dicarboxylic acid*, $C_{15}H_8O_9N_2$, are formed respectively. The latter crystallises from alcohol in slightly yellow needles, melts at 110°, and is dissolved and decomposed by alkali hydroxides or carbonates with formation of formaldehyde and the alkali salt of 5-nitrosalicylic acid; 3-nitro-6-hydroxybenzyl alcohol is probably an intermediate product of the reaction.

o-Nitrophenol is not attacked by formaldehyde. E. W. W.

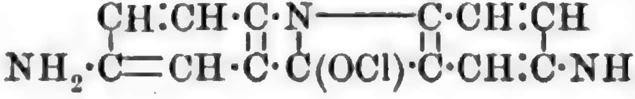
Triketones. II. βγδ-Triketo-δ-phenylbutane. By Franz Sachs and Alfred Röhmer (*Ber.*, 1902, **35**, 3307—3319. Compare Abstr., 1901, i, 670).—The preparation of βγδ-triketopentane has been improved and is described in detail. It gives a yellowish-red to brown coloration with sulphuric acid and benzene containing thiophen; further, it does not form insoluble compounds with sodium sulphite or hydrogen sulphite; both it and its hydrate have a bitter, burning taste and colour the human skin brown. The free keto-group in the *bis*phenylhydrazone (*loc. cit.*) does not react with phenylhydrazine in alcoholic solution or with semicarbazide. The constitution of the 2-acetyl-3-methylquinoxaline previously obtained from the triketopentane and *o*-phenylenediamine hydrochloride is confirmed by the formation of the *phenylhydrazone*,  $C_6H_4<\begin{matrix}N{:}C\cdot CMe{:}N\cdot NHPh\\ N{:}CMe\end{matrix}$, which crystallises in small, lemon-coloured needles and melts at 178°, of the *oxime*, which melts at 194·5°, of the p-*nitrophenylhydrazone*, which melts at 264°, and of the *semicarbazone*, which crystallises from glacial acetic acid and melts at 267—268°. The quinoxaline condenses with benzaldehyde in the presence of sodium ethoxide, forming 2:3-cinnamoylmethylquinoxaline,  $C_6H_4<\begin{matrix}N{:}C\cdot CO\cdot CH{:}CHPh\\ N{:}CMe\end{matrix}$. The bis-*semicarbazone* of the triketopentane crystallises from glacial acetic acid, melts at 221°, dissolves in alkalis, and is reprecipitated by acids. Hydrazine hydrate reacts violently with triketopentane with the evolution of nitrogen and the formation of 4-*hydroxy*-3:5-*dimethylpyrazole*, which crystallises in colourless needles and melts at 173·5°.

βγδ-Triketo-δ-phenylbutane can be prepared by analogous methods to those described (*loc. cit.*). The condensation *product* of benzoylacetone and *p*-nitrosodimethylaniline crystallises from alcohol in reddish-brown needles and melts at 99°. The *triketone*, $COMe\cdot CO\cdot COPh$, is a reddish-yellow oil, is insoluble in water, but miscible with all organic solvents, and is hygroscopic; it gives a violet coloration with sulphuric acid and benzene containing thiophen and reduces Fehling's solution. The *hydrate*, $COMe\cdot C(OH)_2\cdot COPh$, forms colourless rhombic crystals, melts at 54—58°, and is much more stable in air than the triketopentane. The β-*phenylhydrazone* crystallises in dark red, rhombic prisms, melts at 167°, and condenses with *o*-phenylenediamine, forming a *compound*, $C_{22}H_{18}N_4$, which melts at 183°. The triketone reacts with an excess of phenylhydrazine, forming 1:5-*diphenyl*-3-*methylpyrazole*-4-*azobenzene*,  $\begin{matrix}NPh\text{———}N\\ CPh{:}C(N{:}NPh)\end{matrix}>CMe$, which crystallises from alcohol and melts at 136·5°. The β-*monosemicarbazone* of the triketone crystallises in felted needles and melts at 190°. 2-*Acetyl*-3-*phenylquinoxaline* crystallises in colourless needles, melts at 99·5°, and forms a semicarbazone melting at 243° and a *phenylhydrazone* which melts at 183° and is identical with the product obtained from the phenylhydrazone of the ketone and *o*-phenylenediamine; the condensation product of benzaldehyde and the quinoxaline melts at 164°. 4-*Hydroxy*-5-*phenyl*-3-*methylpyrazole* crystallises in white needles and melts at 188°. An undetermined *compound*, obtained by the polymerisation of the ketone in the presence of piperidine, crystallised in broad needles and melted at 202°. R. H. P.

Preparation of Aromatic Guanidines. By FREDERICK J. ALWAY and CAREY E. VAIL (*Amer. Chem. J.*, 1902, **28**, 158—164).—Aromatic guanidines are best prepared by Hofmann's method (*Ber.*, 1869, **2**, 458). The thiocarbamide and amine in molecular proportion are dissolved in alcohol and the solution is heated until it boils; an excess of lead hydroxide is then added and heating is continued until desulphurisation is complete. On the addition of nitric acid to the filtered solution, the nitrate slowly separates and may be collected and recrystallised. In the preparation of phenyldi-*o*-tolylguanidine, a small quantity of tri-*o*-tolylguanidine is simultaneously formed. The yield of the nitrate (or mixture of nitrates) amounts to 75—90 per cent. of the theoretical. The nitrates of the following bases have been obtained by the method described: diphenyl-*m*-tolyl-, phenyldi-*p*-tolyl-, *o*-tolyldi-*p*-tolyl-, *m*-tolyldi-*p*-tolyl-, di-*o*-tolyl-*p*-tolyl-, di-*o*-tolyl-*m*-tolyl-, and phenyl-*o*-tolyl-*p*-tolyl-guanidine.

Diphenyl-*p*-tolylguanidine *nitrate* is obtained in equally good yield from diphenylthiocarbamide and *p*-toluidine, and from phenyl-*p*-tolylthiocarbamide and aniline. It forms small, colourless plates and melts at 196—197°. E. G.

Dyes of the Capri-blue Group. By RICHARD MÖHLAU, K. KLIMMER, and EDMUND KAHL (*Chem. Centr.*, 1902, ii, 377—378; 458—459; from *Zeit. Farb. Textilchem.*, 1902, 1, 313—324, 354—356).—The following compounds are used in the preparation of dyes of the capri-blue or diaminophenazo-oxonium chloride,



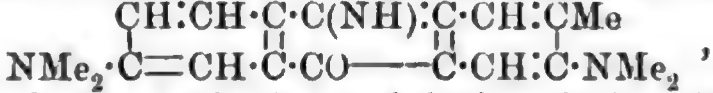
$$\begin{array}{l} \text{CH:CH}\cdot\text{C}\cdot\text{N}\text{———}\text{C}\cdot\text{CH:CH} \\ \text{NH}_2\cdot\text{C}{=}\text{CH}\cdot\text{C}\cdot\text{C(OCl)}\cdot\text{C}\cdot\text{CH:C}\cdot\text{NH}_2 \end{array},$$

group.

4-*Nitro-2-dimethylaminotoluene*, $NO_2\cdot C_6H_3Me\cdot NMe_2$, prepared by nitrating 2-dimethylaminotoluene in concentrated sulphuric acid, boils at 280° with partial decomposition and is readily soluble in acetic acid, mineral acids, or most organic solvents. 4-*Amino-2-dimethylaminotoluene*, $NH_2\cdot C_6H_3Me\cdot NMe_2$, obtained by reducing the preceding compound with tin and hydrochloric acid, is an oil, boils at 248° (uncorr.), is volatile in steam, and readily soluble in acids or organic solvents. The *sulphate*, $C_9H_{14}N_2,H_2SO_4$, separates from alcohol in lustrous crystals and melts at 209°; the *hydrochloride* melts at 208°. The *acetyl* derivative, $NHAc\cdot C_6H_3Me\cdot NMe_2$, crystallises from light petroleum in needles, is readily soluble, and melts at 103°. 2-*Dimethylamino-4-hydroxytoluene*, $NMe_2\cdot C_6H_3Me\cdot OH$, prepared from 4-amino-2-dimethylaminotoluene or by melting potassium 2-dimethylamino-4-sulphonic acid with potassium hydroxide, melts at 46°, boils at 253°, and is readily soluble in acids, alkalis, or organic solvents. The *hydrochloride*, $C_9H_{13}ON,HCl$, forms rhombohedral crystals and melts at 213°. The *acetyl* derivative, $NMe_2\cdot C_6H_3Me\cdot OAc$, is a readily soluble liquid and boils at 195° under 60 mm. pressure. The *benzoyl* derivative crystallises from alcohol in four-sided plates and melts at 46°. By the action of nitrous acid on 2-dimethylamino-4-hydroxytoluene in aqueous solution in presence of excess of hydrochloric acid, dimethylamine and Kostanecki's 3 : 5-dinitrosocresorcinol, $C_6HMeO_2(NOH)_2$ (Abstr., 1888, 263) are formed. On the other hand, by the action of an aqueous solution of sodium nitrite on crystalline 2-dimethylamino-4-hydroxytoluene hydrochloride, a theoretical yield of *5-nitroso-2-dimethylamino-4-hydroxytoluene*, $NMe_2{\cdot}C_6H_2Me(NO){\cdot}OH$, is obtained; it crystallises from benzene in reddish-brown needles, melts at 102°, and is readily soluble in alcohol, benzene, acetic acid, pyridine, or chloroform, and slightly so in water or ether. The *hydrochloride*, $C_9H_{12}O_2N_2,HCl$, melts at 170°, and the *sodium* salt, $C_9H_{11}O_2N_2Na$, forms a blood-red solution in water or alcohol.

The following compounds are prepared from 2-diethylaminotoluene or its derivatives. *4-Nitro-2-diethylaminotoluene* is an oil, boils at 283° (uncorr.), and is volatile in steam. *4-Amino-2-diethylaminotoluene* is a yellow oil which can be distilled at 259° in an atmosphere of carbon dioxide; the *hydrochloride*, $C_{11}H_{18}N_2,2HCl,H_2O$, melts and decomposes at 213—215°. *2-Diethylamino-4-hydroxytoluene* is a slightly yellow oil, becomes red on exposure to air, distils at 259—261° (uncorr.) in an atmosphere of carbon dioxide, and is volatile in steam; by allowing its solution in benzene to evaporate at the ordinary temperature, it separates in crystals which melt at 46°. The *hydrochloride*, $C_{11}H_{17}ON,HCl$, crystallises from alcohol in rhombohedral crystals and melts at 187°. The *benzoyl* derivative crystallises from alcohol in rhombic prisms and melts at 36°. *2-Diethylaminotoluene-4-sulphonic acid*, $NEt_2{\cdot}C_6H_3Me{\cdot}SO_3H,H_2O$, crystallises from water in hexagonal, rhombic plates and is slightly soluble in cold water or alcohol. The *potassium* salt separates from 95 per cent. alcohol in crystals containing water of crystallisation.

Tetramethyldiaminophenotolazo-oxonium chloride, $C_{17}H_{20}ON_3Cl$, is prepared by treating 2-dimethylamino-4-hydroxytoluene with nitrosodimethylaniline in boiling glacial acetic acid. The corresponding *iodide* crystallises from alcohol in violet needles, is slightly soluble in water, and more readily so in alcohol, acetone, or chloroform, forming greenish-blue solutions. By boiling an aqueous solution with alkalis, a blue precipitate is formed and the liquid acquires the odour of dimethylamine. *Tetramethyldiaminophenotoloxazine*,



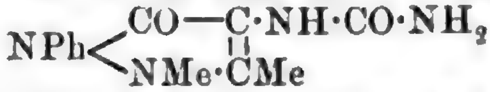
$$\begin{array}{l}\mathrm{CH{:}CH{\cdot}C{\cdot}C(NH){:}C{\cdot}CH{:}CMe}\\ \mathrm{NMe_2{\cdot}C{=}CH{\cdot}C{\cdot}CO{-\!-}C{\cdot}CH{:}C{\cdot}NMe_2}\end{array},$$

prepared by reduction with zinc and hydrochloric acid, is a greyish-white, crystalline powder and is easily reconverted into the dye. *Dimethyldiethyldiaminophenotolazo-oxonium iodide*, $C_{19}H_{24}ON_3I$, prepared from 2-dimethylamino-4-hydroxytoluene and nitrosodiethylaniline, crystallises from alcohol in violet-blue crystals; its solution in water, alcohol, or glacial acetic acid has a more reddish-blue colour than that of the tetramethyl derivative. The isomeric *dimethyldiethyldiaminophenotolazo-oxonium iodide*, prepared from 2-diethylamino-4-hydroxytoluene and nitrosodimethylaniline, forms greenish-blue solutions in water, alcohol, acetone, or glacial acetic acid; it is more soluble in water than the preceding compound and its solution in concentrated sulphuric acid is reddish-violet, whilst that of the isomeride is reddish-brown. Capri-blue, G.O.N., is the corresponding zinc chloride double salt.

Phenyldimethyldiaminophenotolazo-oxonium chloride, $C_{21}H_{20}ON_3Cl$, prepared from dimethylaminocresol and *p*-nitrosodiphenylamine hydrochloride, is a crystalline, indigo-blue powder, soluble in alcohol, acetone, or glacial acetic acid, forming blue solutions, but only very sparingly so in water. Its solution in concentrated sulphuric acid is green, and on dilution becomes violet. as-*Dimethyldiaminophenotolazo-oxonium chloride*, $C_{15}H_{16}ON_3Cl$, obtained by the action of dimethylaminocresol on quinonedichlorodi-imide in alcohol at 40°, crystallises with $1H_2O$, is readily soluble in water, alcohol, acetone, or glacial acetic acid, and forms a very dark violet solution in concentrated sulphuric acid, which, on dilution, becomes successively red, violet, and blue. Sodium hydroxide precipitates the free base from aqueous solutions of the chloride as a reddish-brown substance which is soluble in ether. as-*Dimethyldiaminotolonaphthazo-oxonium chloride*, $C_{19}H_{18}ON_3Cl$, prepared from α-naphthylamine and nitrosodimethylaminocresol hydrochloride, crystallises from water containing hydrochloric acid in green needles and is readily soluble in water, alcohol, acetone, or pyridine, forming blue solutions tinged slightly with red. Its solution in concentrated sulphuric acid is red, and on dilution becomes yellow. The free base, *dimethylaminotolaminonaphthazo-oxonium hydride*, $C_{19}H_{17}O_4N_3$, crystallises from alcohol in orange-red needles.

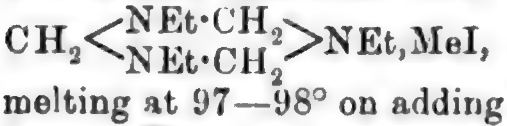
E. W. W.

Antipyrylcarbamide, a Product of the Metabolism of Pyramidone.

By MAX JAFFÉ (*Ber.*, 1902, **35**, 2891—2895. Compare Abstr., 1901, i, 672).—From the urine, after administration of pyramidone, antipyrylcarbamide,  $NPh<\begin{matrix}CO—C\cdot NH\cdot CO\cdot NH_2\\ NMe\cdot CMe\end{matrix}$ (m. p. 247—248°, Knorr, Abstr., 1897, i, 112), has been isolated and identified by conversion into 4-aminoantipyrine; the carbamide gives a violet coloration in aqueous solution with ferric chloride.

K. J. P. O.

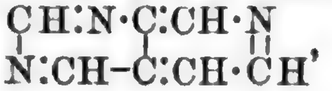
Triethyltrimethylenetriamine.

By ALFRED EINHORN and AUGUST PRETTNER (*Ber.*, 1902, **35**, 2942—2944).—Triethyltrimethylenetriamine combines with methyl iodide forming the *methiodide*,  $CH_2<\begin{matrix}NEt\cdot CH_2\\ NEt\cdot CH_2\end{matrix}>NEt,MeI$, which is obtained as a white precipitate melting at 97—98° on adding ethyl acetate to its solution in chloroform. The triamine yields a *hydriodide*, $C_9H_{22}N_3I$, which crystallises from alcohol in needles, melts at 121°, and, when treated with alkalis, is reconverted into the base. If this hydriodide is heated for three-quarters of an hour at 80—90°, or if an alcoholic solution of the methiodide is boiled, an isomeric *hydriodide* is obtained; this crystallises in clumps of small needles, melts at 199°, and has the properties of a quaternary ammonium iodide.

R. H. P.

Derivatives of Cinchomeronic Acid.

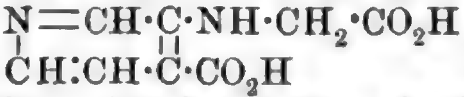
By SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1902, **35**, 2831—2852).—The authors have previously (this vol., i, 401) described derivatives of 2 : 6-benzodiazine, for which they proposed the name copyrine. The present paper deals with derivatives of 1 : 3 : 7-benzotriazine,

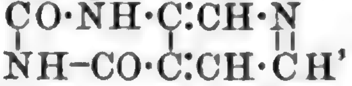


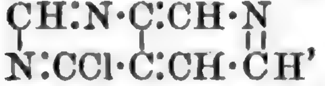
$$\begin{array}{l} \mathrm{CH{:}N{\cdot}C{:}CH{\cdot}N} \\ \mathrm{N{:}CH{-}C{:}CH{\cdot}CH} \end{array},$$

which is named copazoline.

The action of potassium hypobromite on cinchomeronimide is described; the properties of the 3-aminopyridine-4-carboxylic acid obtained differed from those detailed by Blumenfield (Abstr., 1896, i, 60); the melting point varied, according to rate of heating, from 306—310°, the hydrochloride melts and decomposes at 244—245°, and the nitrate at 196—197°. The *methyl* ester crystallises from light petroleum in long, yellowish needles, melts at 86—87°, and forms an *aurichloride* crystallising in yellow needles, and a *platinichloride* forming octahedra-like crystals; its aqueous solution deposits the *hydrate*, $C_7H_8O_2N_2,H_2O$, in long, colourless, silky needles which melt at 50° when quickly heated.

The acid condenses with chloroacetic acid, forming 3-*pyridylglycine*-4-*carboxylic acid*,  $\begin{array}{l} \mathrm{N{=}CH{\cdot}C{\cdot}NH{\cdot}CH_2{\cdot}CO_2H} \\ \mathrm{CH{:}CH{\cdot}C{\cdot}CO_2H} \end{array}$; this crystallises with H_2O in long needles pointed at both ends, decomposes at about 160°, blackens at 180°, and behaves as a monobasic acid. The *silver* salt, $C_8H_7O_2N_2Ag,H_2O$, crystallises in yellowish, pointed needles, and the *barium* salt, $(C_8H_7O_2N_2)_2Ba,H_2O$, is a yellow, crystalline powder.

2 : 4-*Dioxycopazoline*,  $\begin{array}{l} \mathrm{CO{\cdot}NH{\cdot}C{:}CH{\cdot}N} \\ \mathrm{NH{-}CO{\cdot}C{:}CH{\cdot}CH} \end{array}$, obtained when 3-aminopyridine-4-carboxylic acid is heated at 170° with carbamide and also when cinchomerondiamide is treated with bromine and sodium hydroxide, is a yellow, microcrystalline powder, sublimes without melting, and is soluble in dilute acids and fixed alkalis. The *hydrochloride* crystallises in small needles and its aqueous solution gives a blue fluorescence when made alkaline with ammonia. The *platinichloride* crystallises in small, short prisms and the *aurichloride* in golden, flat laminæ, which sinter at 225° and melt and decompose at 246—248°.

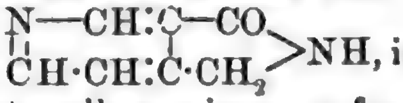
4-*Oxycopazoline*, prepared from aminopyridinecarboxylic acid and formamide, crystallises from water in clusters of needles, sinters at 300°, and melts and partly sublimes at 315—317°; it dissolves in acids and alkalis; the *potassium* salt forms slender needles, the *platinichloride* yellow needles, the *aurichloride* yellow leaflets, and the *nitrate* colourless leaflets. When shaken with a mixture of phosphorus tri- and penta-chlorides at 160°, it yields 4-*chlorocopazoline*,  $\begin{array}{l} \mathrm{CH{:}N{\cdot}C{:}CH{\cdot}N} \\ \mathrm{N{:}CCl{\cdot}C{:}CH{\cdot}CH} \end{array}$, which crystallises from light petroleum in yellowish rods, sinters at 110° and melts at 112°. When the chloro-compound is reduced with a mixture of hydriodic acid and phosphonium iodide at temperatures not exceeding 0°, it yields 3 : 4- (or possibly 1 : 2-) *dihydrocopazoline*, which crystallises from acetone or ether, melts at 144—145°, and forms a strongly alkaline aqueous solution; the *hydriodide*, $C_7H_7N_3,2HI$, crystallises in yellow, pointed needles which decompose at 260—280°, the *platinichloride*, $C_7H_7N_3,H_2PtCl_6$, is an insoluble, orange-yellow, crystalline powder, the *aurichloride*,

$C_7H_7N_3,2HAuCl_4$, crystallises in golden needles, and the *picrate* and *chromate* are both insoluble.

When condensed with acetamide, the aminopyridinecarboxylic acid yields 4-*oxy*-2-*methylcopazoline*, which crystallises from water in long, flat needles melting at 288°, can be sublimed, is soluble in acids and alkalis, and forms a crystalline *platinichloride*.

Cinchomeron 3-*amic acid*, $CO_2H\cdot C_5NH_3\cdot CO\cdot NH_2$, obtained when cinchomeronimide is shaken up for 1 hour with a normal solution of potassium hydroxide, separates from water in clear, rhombic crystals, decomposes at 200°, forming the imide, and when treated with bromine and sodium hydroxide yields 3-aminopyridine-4-carboxylic acid; the *silver* salt crystallises in white leaflets.

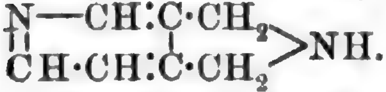
Cinchomerondiamide is best prepared by digesting the imide with alcoholic ammonia and crystallises in transparent cubes and melts at 175—176°, forming the imide; its aqueous solutions deposit the *hydrate*, $C_7H_7O_2N_3,H_2O$, in glassy prisms, which with silver nitrate form the crystalline additive *compound*, $2C_7H_7O_2N_3,AgNO_3$.

When cinchomeronimide is reduced with tin and hydrochloric acid, *cinchomeronimidine*,  $\begin{array}{l}N—CH{:}C—CO\\ CH\cdot CH{:}C\cdot CH_2\end{array}\!\!>NH$, is obtained; this crystallises with H_2O in compact, yellow prisms, or from acetone or ethyl acetate in clusters of yellowish needles; the *platinichloride*,

$$(C_7H_6ON_2)_2,H_2PtCl_6,$$

separates in amber-coloured, octahedral crystals, the *aurichloride* in leaflets, and the *picrate* in needles which darken at 200°; the *hydrochloride*, $C_7H_6ON_2,HCl,H_2O$, crystallises in compact, glassy prisms, which lose their colour at 225° and melt and decompose at 248—250°, and the *stannichloride*, $C_7H_6ON_2,HSnCl_3,H_2O$, crystallises in compact, pointed rods.

Cinchomeronimidine, when heated at 180° with red phosphorus and hydriodic acid, yields a mixture of 4-methylpyridine-3-carboxylic acid, methyl- and dimethyl-pyridine, and a new di-acid base, *merimine*,



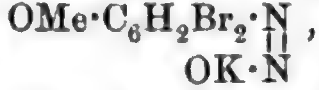
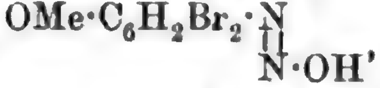
$$\begin{array}{l}N—CH{:}C\cdot CH_2\\ CH\cdot CH{:}C\cdot CH_2\end{array}\!\!>NH.$$

Merimine is an oil, and in aqueous solution is strongly alkaline and absorbs carbon dioxide; the *hydrochloride* forms colourless, flat crystals, the *platinichloride* a yellowish-red powder consisting of needles, the *aurichloride* compact prisms, and the *picrate* an insoluble, crystalline powder which decomposes at 211—212°.

iso*Nitrosocinchomeronimidine* was obtained as a yellow, microcrystalline powder which sublimes when heated and is decomposed by hydrochloric acid, yielding cinchomeronic acid, hydroxylamine, and ammonia. The *platinichloride* is a yellow, crystalline powder, and the *aurichloride* crystallises in small, slender needles. R. H. P.

Isomerism of *anti*Diazo hydrates and Primary Nitrosoamines.

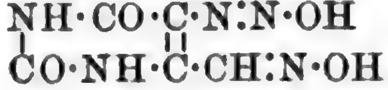
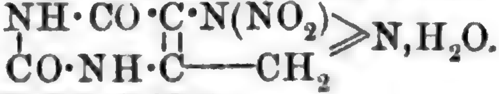
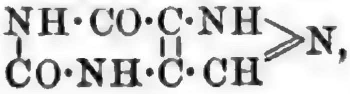
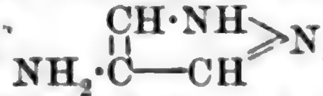
By Arthur Hantzsch and William Pohl (*Ber.*, 1902, **35**, 2964—2978).—The authors show that antidiazotates, $\begin{array}{l}R\cdot N\\ N\cdot OM\end{array}$, when treated with carbon dioxide, yield yellow, primary nitrosoamines, R·NH·NO. The *anti*diazo-hydrates, which are all white when treated with hydrochloric acid, yield diazonium salts, but the nitrosoamines yield hydrochlorides of the type NO·NHR,HCl. A further difference is shown by the rate of coupling, as the antidiazohydrates couple much quicker than do the nitrosoamines.

An aqueous solution of 2 : 6-dibromoanisolediazonium nitrate yields, when treated with an ice-cold concentrated solution of potassium hydroxide, *potassium* syn*diazo*-2 : 6-*dibromoanisole*,  $\begin{array}{l}\mathrm{OMe{\cdot}C_6H_2Br_2{\cdot}N} \\ \qquad\qquad\quad \| \\ \qquad\qquad\mathrm{OK{\cdot}N}\end{array}$, which was obtained as an unstable, white precipitate, and, when treated with a hot concentrated solution of potassium hydroxide, yields the isomeric *potassium* anti*diazo*-2 : 6-*dibromoanisole*, which crystallises in stable needles. The *anti*diazotate, when treated with acetic acid, yields the white 2 : 6-*dibromoanisole*anti*diazo-hydrate*,  $\begin{array}{l}\mathrm{OMe{\cdot}C_6H_2Br_2{\cdot}N} \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad\mathrm{N{\cdot}OH}\end{array}$, which is reconverted into *anti*diazotate when treated with alkalis, and when treated with hydrochloric acid, acetyl chloride, or phosphorus pentachloride yields the diazonium chloride. When the potassium *anti*diazotate, dissolved in ice-cold water, is treated with carbon dioxide, the 2 : 6-*dibromoanisolenitrosoamine*, $\mathrm{OMe{\cdot}C_6H_2Br_2{\cdot}NH{\cdot}NO}$, is obtained; this is an amorphous substance of a deep yellow colour, behaves as a pseudo-acid, and when treated with an ethereal solution of hydrogen chloride, forms a *hydrochloride* which crystallises in small, bright yellow needles.

Benzophenone-p-anti*diazo-hydrate* was obtained as a white, voluminous precipitate, and *benzophenone*-p-*nitrosoamine* as a yellow, unstable substance.

Potassium 2 : 4 : 6-*tribromobenzene*anti*diazotate* crystallises in reddish needles which are very unstable; the corresponding anti*diazo-hydrate* is obtained when an ice-cold solution of *anti*diazotate is acidified with acetic acid, as a white precipitate, which is immediately transformed to the orange-yellow, amorphous 2 : 4 : 6-*tribromophenylnitrosoamine*; this is also obtained when the corresponding diazonium salts are treated with a solution of sodium acetate; it melts and decomposes at 85—86° and forms a light yellow *hydrochloride* and *hydrobromide*. The anti*diazotates*, anti*diazo-hydrates*, and *nitrosoamine*, obtained from 2 : 4 : 6-tribromo-*m*-toluidine, are very similar to the compounds derived from 2 : 4 : 6-tribromoaniline, but are much less stable.

Potassium 2 : 6-*dibromo*-p-*toluene*anti*diazotate* crystallises in long, white needles, the anti*diazo-hydrate* and the *nitrosoamine* are unstable. The analogous *p*-nitro-, *o*-nitro-, and *p*-bromo-compounds were prepared, and are very similar to the substances just described. R. H. P.

Diazo*iso*nitrosomethyluracil and 4-Aminopyrazole. By Georg Wollers and Robert Behrend (*Annalen*, 1902, **323**, 279—283).—Diazo*iso*nitrosomethyluracil may be regarded as having either the constitution  $\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}N{:}N{\cdot}OH} \\ \,| \qquad\qquad \| \\ \mathrm{CO{\cdot}NH{\cdot}C{\cdot}CH{:}N{\cdot}OH}\end{array}$ or  $\left.\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}N(NO_2)} \\ \,| \qquad\qquad \| \\ \mathrm{CO{\cdot}NH{\cdot}C\text{——}CH_2}\end{array}\right\rangle\mathrm{N,H_2O}$. On reduction, it yields *iso*oxanthine,  $\left.\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH} \\ \,| \qquad\qquad \| \\ \mathrm{CO{\cdot}NH{\cdot}C{\cdot}CH}\end{array}\right\rangle\mathrm{N}$, and this substance, when heated with concentrated hydrochloric acid at 150—190°, loses the elements of ammonia and carbon dioxide and becomes converted into 4-*aminopyrazole*,  $\begin{array}{l} CH\cdot NH \\ \| \\ NH_2\cdot C—CH \end{array}\!\!>N$, which is characterised by its *nitrate*, $C_3H_5N_2,2HNO_3,\frac{1}{2}H_2O$, and its *benzoyl* derivative, $C_3H_3N_3Bz_2$; these compounds crystallise in needles, and the latter melts at 173°. G. T. M.

Syntheses with Hippurazoimide. By THEODOR CURTIUS (*Ber.*, 1902, **35**, 3226—3228).—The following compounds have been prepared by condensing hippurazoimide with glycine, $NH_2\cdot CH_2\cdot CO_2H$, or glycylglycine, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$.

Benzoylglycylaminoacetic acid yields a *hydrazide* melting at 227—229° and an *azoimide* melting at 109—110°.

Benzoylglycylglycylaminoacetic acid,

$$NHBz\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

melts at 215—216°, its *ethyl* ester at 173°, its *hydrazide* at 245—250°, and its *azoimide* at 162°.

Benzoylglycylglycylglycylaminoacetic acid,

$$NHBz\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

melts at 235° and its *amide* at 213°. T. M. L.

4-Methylbenzylazoimide. By THEODOR CURTIUS and A. DARAPSKY (*Ber.*, 1902, **35**, 3229—3233).—*p*-Methylbenzylazoimide is stable towards alkalis, but is readily decomposed by acids in a similar manner to benzylazoimide. The decomposition proceeds in four different ways:

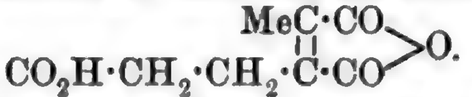
$$\begin{array}{llll}
(1) & C_6H_4Me\cdot CH_2\cdot N_3 \longrightarrow & C_6H_4Me\cdot CH_2\cdot N{<} + N_2 & \longrightarrow \\
 & C_6H_4Me\cdot CH{:}NH \longrightarrow & C_6H_3Me\cdot CHO + NH_3. & \\
(2) & C_6H_4Me\cdot CH_2\cdot N_3 \longrightarrow & C_6H_4Me\cdot CH_2\cdot N{<} + N_2 & \longrightarrow \\
 & C_6H_4Me\cdot N{:}CH_2 \longrightarrow & C_6H_4Me\cdot NH_2 + CH_2O. & \\
(3) & C_6H_4Me\cdot CH_2\cdot N_3 \longrightarrow & C_6H_4Me\cdot CH_2\cdot NH_2 + N_2O. & \\
(4) & C_6H_4Me\cdot CH_2\cdot N_3 \longrightarrow & C_6H_4Me\cdot CH_2\cdot OH + N_3H. &
\end{array}$$

The products actually obtained were hydrazoic acid, *p*-methylbenzyl chloride, *p*-methylbenzaldehyde (converted into the aldazine), ammonia, *p*-toluidine, and *p*-methylbenzylamine. T. M. L.

Azoaldoximes and Hydrazidines. By HUGO VOSWINCKEL (*Ber.*, 1902, **35**, 3271—3274).—Since the composition of phenylazoacetaldoxime has been settled, the constitution of the following substances previously described by the author can be fixed: $C_8H_8O_4N_3Cl$, *p*-chlorophenylazoacetaldoxime (Abstr., 1899, i, 958); $C_8H_{10}ON_3Cl$, *p*-chlorophenylhydrazoacetaldoxime (*ibid.*); $C_9H_{11}ON_3$, *p*-tolylazoacetaldoxime (*ibid.*); $C_9H_{13}ON_3$, *p*-tolylhydrazoacetaldoxime (*ibid.*); $C_{15}H_{14}O_2N_4$, carbanilophenylazoacetaldoxime (Abstr., 1901, i, 53); $C_{10}H_{11}O_2N_3$, acetylphenylazoacetaldoxime (*ibid.*); and $C_{14}H_{10}O_7N_6$, picrylphenylazoacetaldoxime (*ibid.*). The oxygen-free reduction products have been proved to be hydrazidines (amidrazones), and the constitutions of the compounds previously described are: $C_8H_{11}N_3$, phenylethenylhydrazidine, $NHPh\cdot NH\cdot CMe{:}NH$ (Abstr., 1899, i, 958); $C_9H_{13}N_3$, phenylmethylethenylhydrazidine (*ibid.*); and $C_8H_{10}N_3Cl$, *p*-chlorophenylethenylhydrazidine.

Phenylethenylhydrazidine hydrochloride, NHPh·NH·CMe:NH,HCl or NHPh·N:CMe·NH_2,HCl, is obtained by the action of phenylhydrazine on acetimino-ethyl ether in ethereal solution; hydrochloric acid is then added and the ether evaporated. The azidine hydrochloride is separated from the unattacked phenylhydrazine by means of alcohol. It forms silky needles which contain $\frac{1}{2}H_2O$. The hydrated salt melts at 140°, then loses water, and resolidifies, after which it melts at 205°. When a mixture in molecular proportion of this salt and hydroxylamine hydrochloride is left in concentrated aqueous solution with double the molecular quantity of potassium carbonate, slender, orange needles of *phenylazoacetaldoxime* separate. Phenylhydrazoacetaldoxime, when boiled with alcohol to which water has been added, gives, after the addition of hydrochloric acid, *ethenylphenylhydrazidine hydrochloride.* J. McC.

Hæmatin. By WILLIAM KÜSTER (*Ber.*, 1902, **35**, 2948—2954. Compare Abstr., 1901, i, 298).—The anhydride, $C_8H_8O_5$, previously described (*loc. cit.*) is shown to have the constitution



$$\begin{array}{l} \text{MeC}\cdot\text{CO} \\ \quad \| \qquad\quad >\text{O}. \\ \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CO} \end{array}$$

When oxidised, it yields succinic acid, and when reduced by means of hydrogen iodide, a mixture of two isomeric "*hæmotricarboxylic*" *acids* having the constitution of pentane-αγδ-tricarboxylic acids. These were separated by crystallisation from water; the more soluble (1 in 7·3 parts of water at 10°) melts at 140—141° and the other (1 in 75 parts of water at 10°) at 175—176°: the isomeride with the lower melting point is converted into the other form by heating either alone or with water or with hydrochloric acid at 200°. The electrical conductivities of both acids are far less than the conductivities of tricarballylic acids as determined by Zelinsky (Abstr., 1896, i, 349). The isomeride of higher melting point was also obtained from the imide, $C_8H_9O_4N$, previously described (*loc. cit.*).

Acetylhæmin and β-hæmin, when treated with aniline, yield two amorphous products, *hæmeins*, which have the empirical formulæ $C_{34}H_{32}O_4N_4Fe$ and $C_{35}H_{34}O_4N_4Fe$ respectively.

Experiments are described which tend to show that the oxidation with chromic acid of the hæmopyrrole described by Nencki and Zaleski (Abstr., 1901, i, 434) yields the anhydride of methyl-*n*-propylmaleic acid. R. H. P.

Lacto-serum. By ERNST FULD (*Beitr. chem. Physiol. Path.*, 1902, **2**, 425—429).—Lacto-serum (Bordet) is obtained by immunising animals (rabbits in the present research) with milk; their serum then causes a precipitate when added to milk. The reaction is a precipitation of the caseinogen, but the presence of calcium salts is essential, although they may be replaced imperfectly by barium salts. The other proteids are not involved. If the original immunisation is produced with cow's milk, it is only cow's milk or its caseinogen which gives the reaction; goat's milk is easily precipitable with rennet, but not by this lacto-serum; human caseinogen gives scarcely any reaction. A given quantity of lacto-serum can only precipitate a certain quantity of caseinogen. The product has not the same insolubility in salt solution that casein has. Digestion of lacto-serum with a third of its volume of horse-serum has no influence.

W. D. H.

Specific Precipitins. By PHILLIPPE EISENBERG (*Bull. Acad. Sci. Cracow*, 1902, 289—310).—The experiments were performed by immunising rabbits against egg-albumin and horse-serum. A suggestion for quantitative work on the 'precipitins' obtained is to take measured quantities of the serum diluted so that it only just gives the reaction. The amount of precipitin 'absorbed' means that which takes part in the process of precipitation. The 'precipitin' has many of the characters of coagulated albumin and contains both precipitin and 'precipitable substance,' but not all of either. An excess of both is present which can be detected by a further precipitate occurring when more of either substance is added. Excess of 'precipitable substance' inhibits precipitation; this is attributed to an inhibitory substance in the 'precipitin.' All immune substances are not contained in the pseudo-globulin fraction, but were found also in the eu-globulin fraction of the serum. W. D. H.

Action of Superheated Steam on Keratin. By RICHARD BAUER (*Zeit. physiol. Chem.*, 1902, **35**, 343—357. Compare Krukenberg, *Sitzungsber. Jena Ges. Naturwiss.*, 1886).—When keratin, obtained from horn shavings, is heated with water in sealed tubes at 150° for 24 hours, considerable amounts of hydrogen sulphide and a second volatile sulphur compound, presumably methyl mercaptan, are formed. The solution contains two compounds corresponding with Neumeister's atmidalbumin and atmidalbumose, which the author terms *atmidkeratin* and *atmidkeratose*. They are most readily obtained by concentrating the solution and saturating it with powdered sodium chloride when atmidkeratin is precipitated. The filtrate from this precipitate, on treatment with hydrochloric acid saturated with sodium chloride, yields first a mixture of the two compounds and then atmidkeratose.

The compounds are only slowly acted on by pepsin and trypsin.

J. J. S.

Glutinpeptone. By W. FAHRION (*Chem. Zeit.*, 1902, **26**, 675—677). —Glutinpeptone, obtained by warming animal hide or gelatin with alcoholic sodium hydroxide, is strongly basic. Unlike its hydrochloride, it is insoluble in alcohol. The saponification number increases with the duration of warming with alkali; the increase is more rapid in aqueous solution than in aqueous-alcoholic solution. The saponification number is lower when air is completely excluded than when it has free access to the solution. From this behaviour, it is concluded that glutinpeptone contains no alcoholic hydroxyl groups, and that it is not an aldehyde, ketone, or lactone. A determination of the equivalent of uric acid showed that it increases in the same way as that of glutinpeptone; from this, it is assumed that the high value of the saponification number of glutinpeptone on prolonged heating is due to the presence of imino-groups united to carbonyl groups.

When glutinpeptone is oxidised in alkaline solution with potassium permanganate, a substance is obtained which is insoluble in alcohol, but which gives a soluble hydrochloride; at the same time, butyric acid is formed, and a very small quantity of benzoic acid.

Glutinpeptone scarcely absorbs iodine, indicating that it does not contain doubly-linked carbon atoms in an open chain. J. McC.

Nucleic Acid from Embryos of Wheat. By THOMAS B. OSBORNE and ISAAC F. HARRIS (*Zeit. physiol. Chem.*, 1902, **36**, 85—133. Compare Abstr., 1900, i, 573).—The embryos of wheat contain relatively large amounts of a nucleic acid which the authors term *triticonucleic acid*. Some 3·5 per cent. of the acid is contained in the commercial flour freshly obtained from wheat embryos, but the amount rapidly diminishes when the flour is kept. The acid has most of the properties characteristic of the nucleic acids of animal origin, but is much less readily soluble in water. Its percentage composition agrees best with the formula $C_{41}H_{61}O_{31}N_{16}P_4$. It forms *acid potassium*, *sodium*, and *ammonium* salts, which are soluble in water, yielding solutions with strongly alkaline properties, and it is found to be practically impossible to obtain the acid free from mineral matter.

When hydrolysed with mineral acids, triticonucleic acid yields guanine (1 mol.), adenine (1 mol.), uracil (2 mols.), and pentoses (3 mols.).

The *silver* salt contains six atoms of silver, and the free acid presumably contains six hydroxyl groups. It is suggested that the acid is formed by the condensation of four $P(OH)_5$ groups, the four atoms of phosphorus being united with the aid of three oxygen atoms. When boiled for a short time with dilute acids, only one-fourth of the total phosphorus is obtained in the form of orthophosphoric acid, and a complex phosphorus acid is produced by the elimination of one atom of phosphorus together with guanine, adenine, and a molecule of pentose.

Triticonucleic acid may be identical with the nucleic acid obtained from yeast and somewhat resembles guanylic acid. J. J. S.

***allo*Oxyproteic Acid, a Normal Constituent of Urine.** By STANISLAUS BONDZYŃSKI and K. PANEK (*Ber.*, 1902, **35**, 2959—2963).—Analyses are given of the *barium* and *silver* salts of a new acid, allo*oxyproteic acid*, which the authors have isolated from urine. The acid contains carbon, hydrogen, oxygen, nitrogen, and sulphur, appears to be a normal constituent of urine, and is very similar to oxyproteic acid (Abstr., 1898, i, 501); it does not give the typical reactions of proteids, and has not yet been isolated in the pure state.

R. H. P.

Isolation of Malt Enzymes and the Proteolytic Enzyme of Malt. By CARL J. LINTNER (*Chem. Centr.*, 1902, ii, 288—289; from *Zeit. ges. Brauw.*, **25**, 365—368).—The malt enzymes are best isolated by salting out with ammonium sulphate. The small precipitate first obtained on addition of the sulphate has a distinct diastatic, but scarcely any proteolytic, action; the active enzyme is precipitated on further addition of the sulphate. The enzymes isolated by this means are capable of liquefying gelatin and have a diastatic action or fermentative power of 143, whilst that of the enzyme obtained by precipitation with alcohol seldom rises above 80. The experiments confirm the presence of a proteolytic enzyme in malt, but do not indicate that it plays any important part in the mashing process. The assumption that it resembles trypsin and determines the decomposition of proteids during germination is unfounded. When liquefied gelatin is digested with the enzymes for 48 hours at 40°, the glutin is scarcely attacked, and only a very slight peptonisation could be detected by means of the biuret reaction. The fermentative action of the enzymes should rather be compared with that of malt extracts which have been attenuated by heating and which, although capable of liquefying starch paste, are unable to convert the starch into sugar.

E. W. W.

Yeast-gum and Invertase. By KINTARO OSHIMA (*Zeit. physiol. Chem.*, 1902, **36**, 42—48. Compare Salkowski, Abstr., 1894, i, 221, 316; 1895, i, 166; 1901, i, 180).—When yeast gum is distilled with hydrochloric acid of sp. gr. 1·060, the distillate gives the reaction for methylfurfuraldehyde (Abstr., 1901, ii, 484) and the original gum presumably contains a methylpentosan. When the gum is hydrolysed with sulphuric acid, the chief product is *d*-mannose.

Attempts were made to purify crude invertase (Osborne, Abstr., 1899, i, 967). If the extraction with chloroform at 34° is continued for several days, the yield of invertase is somewhat better, but the product contains larger amounts of gum.

A considerable amount of the gum is thrown down in the first fraction when the clear chloroform extract is fractionally precipitated with 93 per cent. alcohol. A simpler method for the removal of gum is to precipitate the invertase from a neutral solution of Osborne's crude product with a 5 per cent. solution of copper acetate, to wash thoroughly, precipitate the copper as sulphide, and to pour the filtrate, freed from hydrogen sulphide, into alcohol. J. J. S.

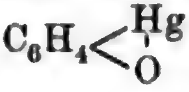
Invertase of Yeast. Quantitative Experiments on the Action of Alcohol and Acids on this Enzyme. By THOMAS BOKORNY (*Chem. Zeit.*, 1902, **26**, 701—703. Compare Abstr., 1901, ii, 568).—The author's experiments demonstrate that the inverting action of yeast is not effected by the living protoplasm, but by a material which can be separated from the yeast cell: this view was originally expressed by Berthelot in 1860. Four grams of fresh yeast extract at 45—50° in 15 minutes can convert from 68 to 82 per cent. of a sucrose solution varying in strength from 5 to 20 per cent. Dried yeast has in no way lost this power. When kept for several days under absolute alcohol at the ordinary temperature, the inverting action of yeast is unimpaired, but at 45° it is completely destroyed. Similarly, 5 per cent. formaldehyde has little effect at the ordinary temperature, but destroys the inverting power at 45°. Dried yeast extract is changed but little as regards inverting power by keeping in 0·5 per cent. oxalic acid, 0·5 per cent. hydrofluoric acid, 2 per cent. acetic acid, or 2 per cent. lactic acid.

K. J. P. O.

[Formation of Aromatic Mercury Compounds.] By Leone Pesci (*Zeit. anorg. Chem.*, 1902, **32**, 227—234. Compare Abstr., 1898, i, 648; 1901, i, 576).—A claim for priority against Dimroth (this vol., i, 656). The author also defends the views he has expressed previously on the constitution of the compounds obtained from aniline and mercuric acetate and other mercury aromatic compounds against Dimroth's criticisms.

J. McC.

[Formation of Aromatic Mercury Compounds.] By Otto Dimroth [and, in part, Richard Metzger] (*Ber.*, 1902, **35**, 2853—2873. Compare Abstr., 1899, i, 154, 428, and this vol., i, 656).—The hydroxyphenylmercury salts (previously described) dissolve in dilute sodium hydroxide; carbon dioxide precipitates from the solution of the ortho-compound the internal anhydride of *o*-hydroxyphenylmercury hydroxide,



$C_6H_4{<}\begin{matrix}Hg\\|\\O\end{matrix}$; from the para-compound, an *oxide*,

$$(OH{\cdot}C_6H_4{\cdot}Hg)_2O,$$

is obtained as an insoluble, white powder which cannot be converted into *o*-phenylenemercury oxide.

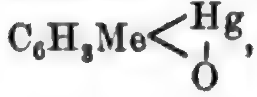
The pharmaceutical preparation, *Hydrargyrum carbolicum*, which is prepared by heating sodium phenoxide and mercuric chloride in alcoholic solution, and is generally considered to be a mercury phenoxide, is now shown to consist mainly of a mixture of *o*- and *p*-hydroxyphenylmercury oxides and hydroxyphenylenedimercury oxide.

o-*Mercuryphenol*, $(OH{\cdot}C_6H_4)_2Hg$, is prepared by treating *o*-hydroxyphenylmercuric chloride with sodium thiosulphate; it crystallises in lustrous, white plates, which become coloured on heating and dissolve in alkali hydroxides, but not in carbonates. The hydroxyphenylmercury salts give, with nitrous acid, at first coloured solutions and then coloured precipitates which resemble those obtained by the action of Millon's reagent on phenols, proteids, &c.

p-Cresol and mercuric acetate, in mol. proportion, give equal quantities of a mono- and a di-mercury compound; at 100°, only the dimercury compound is formed; p-*cresolmercury acetate*,

$$OH{\cdot}C_6H_3Me{\cdot}Hg{\cdot}OAc,H_2O,$$

is obtained by crystallising the product of the reaction from acetic acid; it decomposes at 200°; addition of sodium chloride to the mother liquor precipitates p-*cresolmercury chloride*, $OH{\cdot}C_6H_3Me{\cdot}HgCl$, which crystallises in needles melting at 166° and decomposing at 176°, when it becomes solid. The corresponding *iodide* is prepared from the chloride and potassium iodide, and crystallises in slender needles which begin to decompose at 145°; the *acetate*, prepared by dissolving the oxide in acetic acid, crystallises in leaflets melting and decomposing at 163°. The *oxide*,



$C_6H_3Me{<}\begin{matrix}Hg\\|\\O\end{matrix}$, is prepared as a white powder by dissolving the chloride in dilute sodium hydroxide and then precipitating with carbon dioxide; the *sodium* salt, $ONa\cdot C_6H_3Me\cdot Hg\cdot OH$, crystallises in very soluble needles. The *benzoyl* derivative, $OBz\cdot C_6H_3Me\cdot HgCl$, prepared by the Schotten-Baumann method, crystallises in slender needles melting at 241—242°.

o-*Iodo*-p-*cresol*, $OH\cdot C_6H_3MeI$, is prepared by the action of iodine on the iodide previously mentioned; it crystallises in hair-like needles melting at 35° and boiling at 117° under 12 mm. pressure.

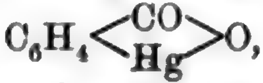
Benzenediazonium chloride reacts with *o*-phenylmercury chloride, forming the *azo*-compound, $N_2Ph\cdot C_6H_3(OH)\cdot HgCl$, which is a reddish-brown powder melting at 147°; it forms a stable *additive* product with 1 mol. of acetic acid, which crystallises in yellowish-brown needles melting at 126—128°; a hydrate with 1 or $1\frac{1}{2}H_2O$, is obtained when water is added to the alcoholic solution and crystallises in slender, yellow needles, which lose water when dried over sulphuric acid, forming a very hygroscopic, red powder; when dried at 100°, a red powder is obtained which is no longer hygroscopic. The azo-compound just mentioned combines with acids; the *compound* with hydrogen chloride is a red powder melting at 160°. When the azo-compound is boiled with hydrochloric acid, it is converted into *p*-hydroxyazobenzene. *p*-Hydroxyphenylmercury chloride and benzenediazonium chloride yield mainly *p*-hydroxyazobenzene together with a small quantity of a *substance*, probably benzeneazo-*p*-hydroxyphenylmercury chloride; the latter melts at 130—131°, and forms a crystalline additive product with one mol. of acetic acid. Hydroxyphenyldimercury acetate and the diazonium chloride give chiefly *benzeneazo*-o-*hydroxyphenylmercury acetate*; it crystallises in yellow prisms melting at 197—198°; *benzeneazohydroxyphenyldimercury chloride*, as an additive product with 1 mol. of acetic acid, was also isolated by precipitating with sodium chloride and crystallising the product from acetic acid; it melts and decomposes at 165—170°. *Benzeneazo*-p-*cresolmercury acetate*, $N_2Ph\cdot C_6H_2Me(OH)\cdot Hg\cdot OAc$, forms red needles melting and decomposing at 269°; the *chloride*, prepared from the acetate, crystallises in yellowish-brown, silky needles melting and decomposing at 249°; both these compounds are soluble with difficulty in alkalis.

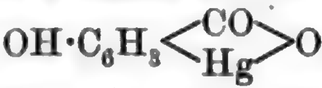
Thymolmercury chloride, $OH\cdot C_6H_2MePr\cdot HgCl$, is prepared by adding sodium chloride to the acetic acid solution of the product of the reaction of mercuric acetate and thymol; it crystallises in needles melting at 139·5°; the *sodium* salt forms needles; *thymoldimercury acetate*, $OH\cdot C_6HMePr(Hg\cdot OAc)_2$, separates directly from the product of the reaction of thymol and mercuric acetate, and forms needles melting and decomposing at 215—216°; the *sodium* salt crystallises in leaflets.

A mixture of resorcinolmercury chloride and resorcinoldimercury chloride is obtained by adding sodium chloride to the product of the interaction of mercuric acetate and resorcinol; chloroform extracts the *monomercury* compound, $C_6H_3(OH)_2\cdot HgCl$, which crystallises in prisms containing chloroform and melts at 105°; when free from chloroform, it melts at 123°; it is decomposed by water, and yields a solution in sodium hydroxide, rapidly becoming coloured. *Resorcinoldimercury chloride* forms an insoluble, white powder which begins to decompose at 200°. Quinol does not form a mercury compound, but is oxidised to quinhydrone by mercuric acetate.

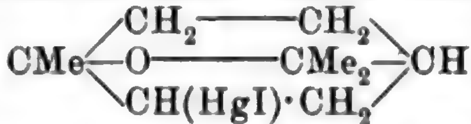
Phenol ethers, such as anisole, and phenetole, react with mercuric acetate less readily than the phenols, and yield substances which have previously been described.

o-*Benzophenonemercury chloride*, $COPh\cdot C_6H_4\cdot HgCl$, is prepared by heating together dry mercuric acetate and excess of benzophenone, converting the acetate thus formed into chloride by means of sodium chloride, and separating the insoluble dimercury compound by ether; the monomercury compound, crystallises in leaflets melting at 167—168°; the *dimercury* compound is a yellowish powder. o-*Benzophenonemercury bromide* melts at 176°, and is converted by bromine into *o*-bromobenzophenone (m. p. 35°). Acetophenone and mercuric acetate yield *phenacylmercury chloride*, $COPh\cdot CH_2\cdot HgCl$, the nucleus not being attacked; this substance forms needles melting at 145—146°, and is easily decomposed by bromine, giving phenacyl bromide.

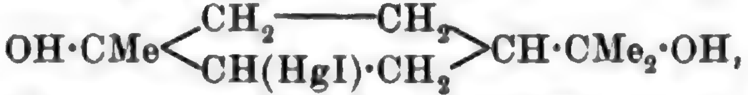
Anhydrous mercuric benzoate is obtained from the hydrated salt by crystallisation from chloroform; it forms crystals melting at 165°; when heated at 170°, it is converted into a *compound*,  $C_6H_4\left<\begin{smallmatrix}CO\\Hg\end{smallmatrix}\right>O$, which forms a powder soluble in alkali hydroxides and carbonates, and is changed by sodium chloride into *chloromercuribenzoic acid*; when treated with bromine, *o*-bromobenzoic acid is formed.

When dry mercuric salicylate is heated at 100°, it is converted into salicylic acid and a *compound*,  $OH\cdot C_6H_3\left<\begin{smallmatrix}CO\\Hg\end{smallmatrix}\right>O$, which is the anhydride of *o*-hydroxymercurisalicylic acid; it is a white powder, soluble in alkalis, and identical with the pharmaceutical preparation, *Hydrargyrum salicylicum*. By iodine, it is converted into *o*-iodosalicylic acid, consequently the mercury is attached to the benzene nucleus in the ortho-position relatively to the hydroxyl group. K. J. P. O.

Mercuric Compounds from Terpineol and Dimethylheptenol. By JULIUS SAND and FRITZ SINGER (*Ber.*, 1902, 35, 3170—3187).—Characteristic products cannot be obtained by shaking ethereal terpineol with aqueous mercuric nitrate or sulphate; crystalline products can, however, be obtained by dissolving yellow mercuric oxide in 20 per cent. nitric acid, adding potassium hydroxide until basic nitrate begins to separate, and shaking with ethereal terpineol solution, the alkali and terpineol being added alternately until mercurous oxide begins to be precipitated; the solution is made strongly alkaline, and on addition of potassium iodide gives an immediate precipitate of mercuricineol iodide, a gradual separation of α-mercuric *trans*-terpin iodide from the filtrate, and a further separation of β-mercuri-*trans*-terpin iodide on passing carbon dioxide into the solution.

Mercuricineol iodide,  $\mathrm{CMe}\left<\begin{matrix}\mathrm{CH_2}\text{——}\mathrm{CH_2}\\ \text{—O——}\mathrm{CMe_2}\text{—}\\ \mathrm{CH(HgI)\cdot CH_2}\end{matrix}\right>\mathrm{CH}$, crystallises from alcohol in small, glistening prisms, dissolves very readily in cold benzene or chloroform, becomes yellow at 115°, and melts and decomposes at 152—154°. The *chloride* crystallises from alcohol in white, felted needles, melts constantly and sharply at 162°, and, unlike the iodide, is readily soluble in alkali. The iodide does not yield a benzoate, and when reduced with sodium amalgam does not yield a terpineol, but a mobile oil, which gives precipitates with hydrogen chloride, bromide, and ferrocyanide, and is therefore in all probability cineol.

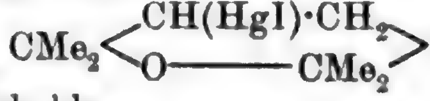
a-Mercuri-trans-*terpin iodide*,



$$\mathrm{OH\cdot CMe}<\begin{matrix}\mathrm{CH_2{-}{-}{-}CH_2}\\ \mathrm{CH(HgI)\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH},$$

separates from benzene in glistening, colourless prisms, is sensitive to light, becomes red at 120°, and melts and decomposes at 144°. It combines with alcohol to form the *alcoholate*, $C_{10}H_{19}O_2IHg,C_2H_6O$, which crystallises from alcohol in glistening needles, and becomes red and melts at 123—125°. The iodide is reduced by sodium amalgam, or by electrolysis at a platinum cathode, to *trans*-terpin (m. p. 156°).

β-Mercuri-trans-*terpin iodide* melts at 38°, separates from organic solvents as an oil, and, like the preceding compound, is reduced by sodium amalgam to *trans*-terpin; when boiled with organic solvents, it is readily converted into the stable α-compound. The α- and β-compounds are probably stereoisomerides, differing only in the position of the –HgI group; as the α-compound is readily reconverted into terpineol by mineral acids, it probably has the –HgI group in the *cis*-position relatively to the adjacent hydroxyl, whilst the β-compound, which is only slowly decomposed, would have the –HgI in the *trans*-position.

Dimethylheptenol, $\mathrm{CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH}$, prepared by Grignard's method from methylheptenone and magnesium methiodide, is a highly refractive oil, and boils at 85—86° under 14 mm. pressure (uncorr.). Towards mercury salts, it behaves in just the same way as terpineol, giving an *iodide*, $C_9H_{17}OIHg$, which is insoluble in alkalis, and probably has the structure,  $\mathrm{CMe_2}<\begin{matrix}\mathrm{CH(HgI)\cdot CH_2}\\ \mathrm{O{-}{-}{-}CMe_2}\end{matrix}>\mathrm{CH_2}$, together with an *iodide*, $C_9H_{19}O_2IHg$, probably

$$\mathrm{OH\cdot CMe_2\cdot CH(HgI)\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH},$$

soluble in alkalis, which separates from benzene in glistening crystals, becomes yellow and melts at 124—125°, and probably also an isomeric oily iodide, $C_9H_{19}O_2IHg$.

T. M. L.

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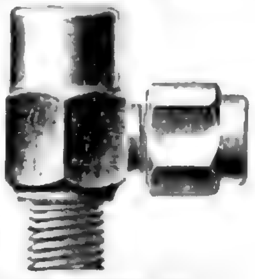

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INTRODUCTORY PREFACE

THE manipulation of gases has been the object of attention at various epochs of chemical history. Scheele collected his gases in bladders; Priestley, unconsciously imitating Mayow, brought the pneumatic trough into use; and Bunsen devised processes still employed in analysis of gases. The device of Sprengel's pump, and later that of Töpler, has placed a new instrument at the disposal of chemists; and the ingenious methods of Hampson and Linde of producing liquid air in quantity has made it possible to deal with gases as easily, if not more so, as with liquids. In the research on the gases of the helium series a number of workers, including Lord Rayleigh, and Drs. Collie and Travers, have made use of apparatus, a description of which does not always appear in the original papers on the subject, but which will be found treated of in this volume. Dr. Travers has also taken the opportunity of tabulating the more important constants relating to gases; and what is perhaps of still greater moment, of directing the attention of chemists and physicists to lacunæ in knowledge, which suggest subject for research.

WILLIAM RAMSAY.

PREFACE

IN the following pages I have attempted to give an account of the experimental methods which have been applied to the study of gases, and to describe the more important researches which have been carried out with a view to determining their properties.

It is probable that in no other section of chemistry or physics do such discrepancies occur as exist among the experimental values assigned by different investigators to the physical constants relating to gases. The existence of such irregularities renders the treatment of the subject rather difficult; and as in many cases the methods of manipulation, and the manner in which the gases experimented upon were prepared, are only briefly described in the original papers, it is often impossible to arrive at the probable sources of error. In stating results I have in many instances attempted to indicate to what extent they may be relied upon.

The breadth of the subject does not permit of its complete treatment within the limits of a single volume. I have therefore been obliged to restrict myself to a description of such methods as may find application in research, and of those investigations which either involve new principles, or which lead to results of importance. In the chapters which deal with the liquefied gases, of which our knowledge is daily increasing, statements are made which may shortly need revision. This is particularly the case with regard to experimental results which involve measurements of temperature, for until we arrive at a more certain knowledge of the relationship between the practical thermometric and thermodynamic scales of temperature, the values of physical constants at low temperatures must retain a more or less empirical character.

A considerable portion of the book is devoted to the description of the methods which have been developed during the investigation of the gases of the helium group, and which are capable of application to the study of other problems. The opening up of this new field of research we owe to Professor William Ramsay, and I take this opportunity of thanking him for that training and experience in experimental science which I have gained while working with him at University College.

To Professor J. Norman Collie, to Mr. E. C. C. Baly, and to Dr. F. G. Donnan, I am much indebted for the advice and assistance they have rendered me. I also wish to express my most sincere thanks to Mr. George Senter, B.Sc., for revising the final proof-sheets of the book.

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The attention of authors is directed to the following resolution of the Council.

"No communication shall be included in the list of titles of papers to be brought before a Meeting of the Society, unless it is in the hands of the Secretaries **at least three days** before the date of the Meeting; and no announcement of titles can be made in the Proceedings until the communications have been received by the Secretaries."

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As the **Illustrations** for the Journal (including curves) are, as far as possible, executed in photographic "process" work, the drawings, &c., accompanying the papers **must be carefully done on a large scale on smooth white Bristol board in Indian ink, so as to admit of the blocks being prepared directly from the drawings.**

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